

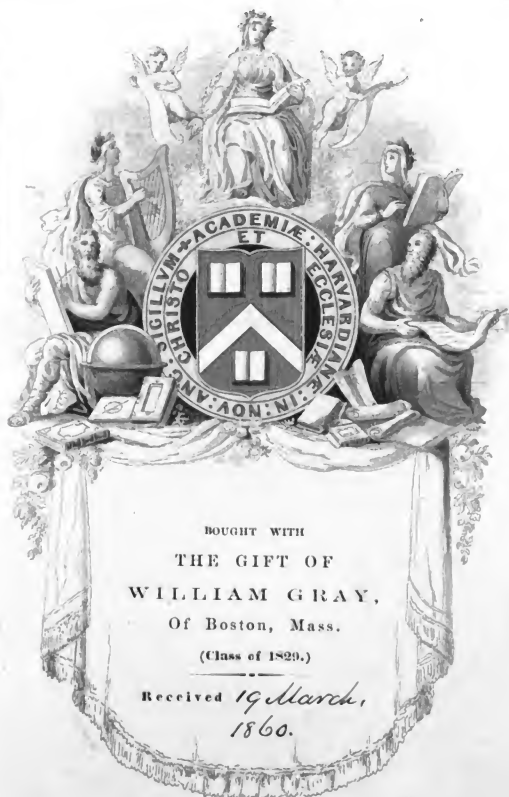
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THE
QUARTERLY JOURNAL
OF THE
CHEMICAL SOCIETY.

I.—*Investigation of the Vegetable Tallow from a Chinese Plant,
the "Stillingia sebifera."*

By NEVIL STORY MASKELYNE, M.A., F.G.S.

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OXFORD.

THE investigation now offered to the Chemical Society has been long made, as regards its most important features, but was not before published from a want of completeness in its details. That completeness has been now effected, and methods, introduced subsequently to the period of the original investigation, have been employed to establish its correctness.

Chinese vegetable tallow is a substance used, I believe, already in considerable quantities in the candle manufactures of this country, though the specimens first employed for this investigation were from the earliest imported cargo of it. It has been made the subject of examination by three chemists. Thomson and Wood,* and M. v. Börck,† have detailed the results of their labours upon it. The former two chemists imagined that they had established the nature of the solid fat acid in the Chinese tallow as consisting in a mixture of margaric and stearic acids;‡ the latter, that he had shown it to be a new acid, to which he gave the name of stillistearic acid. That both arrived at erroneous conclusions will be seen from the following pages.

M. Börck has given an account§ of the vegetable tallow itself, which is so complete that I am able to add nothing to it.

* J. pr. Chem. xlvii. 240.

† Ibid. xlix. 395.

‡ Since this paper was read I have received from Dr. Thomson specimens of the fat he examined, and of the acid he obtained from it, which render it evident that this fat was not the same with the tallow I have described in this paper.

§ Chem. Gaz. 1850, p. 647.

The *Stillingia sebifera*, the O ka O of the Chinese, bears berries which are about a half-inch in length, united together in threes, surrounded by a triple capsule, which detaches itself very readily from the fruit. These berries consist of a stone-fruit, the kernel of which is protected by a hard shell, which again is coated by an envelope of cellulose substance, perhaps a quarter of an inch thick, in the cells of which the tallow is contained. This tallow-bearing envelope is estimated at about 25 per cent. of the fruit. The tallow is pressed out from the fruit by the Chinese, melted on water, and cast into large cylindrical moulds with a Chinese stamp on them. There is another product, a fluid fat, which is procured out of the more solid portion, and which does not come into commerce.

The tallow of commerce, when freshly cut, is white, and becomes yellowish-brown by exposure. It possesses a faint but peculiar smell, calling to mind at once its fatty nature and vegetable origin. Its behaviour with solvents is as follows. The liquid portion of the tallow (its oleine) being soluble in the cold in various menstrua, imparts to them a solvent action on the solid portion also, which they otherwise do not possess; and hence, not only do oil of turpentine and coal-naphtha dissolve it entirely, but it is also partially soluble in ether, in equal parts of ether and absolute alcohol, ether and common alcohol, wood-spirit, absolute alcohol, and common "strong alcohol." The order in which I have placed these menstrua indicates the order of solubility, which is, of course, inversely as the amount of solid fat which remains undissolved. On boiling, it is completely dissolved by ether, by ether and absolute alcohol (equal parts), ether and common alcohol, absolute alcohol, wood-spirit, and in common alcohol,—the facility of solution being indicated by the order of the solvents.

The ethereal solutions remain clear after cooling, and only ultimately deposit the cauliflower crystals, which are formed immediately in the other solutions. Heated in a capillary glass tube, it melts at 37° C., and beginning to solidify at 32° C., is finally hard at 26° C. But if carefully melted in a test-tube, the fresh tallow, or this after it has been melted and very slowly cooled, has a melting-point as high as 44° C. The melted tallow has an acid reaction. This might be due to a decomposition of the fat-salts in the tallow, or, again, it might be the result of an acid fat-salt. That it was not due to the former is rendered probable by the absence of glycerine from water on which the tallow had been kept for some time melted, the evaporation of this water yielding no acroleine odour.

When, however, the tallow has been so boiled on water, it imparts

to it a strongly acid reaction and smell; in fact, the water removes from the tallow itself this acid character, sufficiently showing that it is not to a salt of acid constitution that the acidity is due. This acid may be separated from the tallow by boiling it with absolute alcohol, and pressing out the alcohol on its cooling, the lead-salt being now readily precipitated from the alcoholic solution by acetate of lead as a fine white salt. The saponified tallow, moreover, when treated with tartaric acid and distilled, yields an acid distillate, which proves the acid to be volatile. In fact, if the tallow be melted in a flask on the water-bath, it yields an acid smell, and vapours of acid reaction, and there is nothing of the character of acroleine in the odour, but rather that of acetic or propionic acid. The aqueous solution yields a baryta-salt, which is soluble in water.

This volatile acid is present in the tallow in very small quantity, and was not further investigated. In other respects, the chemical nature of this tallow is briefly told: it consists of palmitine and oleine, and is perhaps the best known source for the chemist of palmitic acid: But, since the former of the two memoirs to which I have referred is written on the idea that this substance contains margarine and stearine, and the latter gave the history of a new acid, it became important to establish the true character of the acid with care and precision.

The original method followed for this purpose consisted in taking a considerable quantity of the tallow, melting it, and, while warm, pressing it out in linen or canvas. The part remaining on the linen, and melting at 48° — 49° C., should, of course, contain in a preponderating amount the constituent of the tallow yielding the acid of the highest melting-point, while the portion pressed out, and which melted at 30° — 32° C., should contain the constituent yielding any acid of lower melting-point. The former yielded in fact an acid, by saponification and decomposition of the soap, melting at 60° C., and this, by repeated crystallisations from alcohol, was raised to a melting-point of 63° C. The melting-point of the acids procured from the pressed-out portion was 53° C.; but continual crystallisations will raise this to the same melting-point as the former. This second portion, therefore, also contains the acid of the highest attainable melting-point.

This pressed-out part of the tallow was therefore again melted, and pressed out when partially cold, and this *second* pressed-out portion was saponified, and the acids separated by hydrochloric acid. A mixture of acids was thus obtained, and it remained to ascertain whether this mixture contained any other acid than the one mentioned, whose melting-point was 63° C., and oleic acid. Accordingly the fat-acids

were dissolved in alcohol, and the incipient deposit of crystals separated by filtration—the filtrate being similarly treated several times in succession—part of the alcohol being evaporated off as the solution became less rich in the more solid fat. The crystals in each case were at the time pressed and blotted, and then separately saponified, as were also the finally remaining acids in the filtrate from the whole.

Each mass was then carefully dissolved in alcohol, and allowed to crystallise, and then filtered and pressed to rid it of oleate, and after a repetition of this process two or three times, the acids were recovered, and found all to possess a melting-point within a degree of one another, viz. 62° — 63° C. The acids were then mixed in such a way as that the first separated in the process I have described were thrown together, and so on with the others, so that the acids [I.] [II.] [III.] and [IV.] represent in order the bodies which should be expected to contain respectively from more to less of the supposed higher acid. Furthermore, the acid from the filtrates, as before described, formed [V.] in the series. The ammonia-salts, and from these the several silver-salts, were made; and silver determinations and analyses of these will be found in their proper place.

Subsequently, however, to the experiments which are above very briefly described (for their detail would now be too long, and not of the same interest in description as formerly), the method of fractional precipitation introduced by Heintz was adopted, to confirm the absence of any second solid fat-acid. A large amount of the vegetable tallow was saponified by an alcoholic solution of potash, water added to the clear solution, and the alcohol distilled off. The acids separated from the soap by hydrochloric acid, and carefully washed in boiling water, were next dissolved in a large amount of alcohol, and mixed with a small quantity of acetate of lead. A slight cloudiness in the liquid is cleared immediately by a drop or two of acetic acid, but, on cooling, the lead-salt crystallises in minute white scales. This is filtered, and the filtrate treated with a fresh dose of lead-salt. The whole of the solid acid is thus thrown down by the lead-salt, after which an excess of ammonia is requisite to effect the formation of any further precipitate, which, however, when so formed, consists only of the yellow oleate of lead. The white salts precipitated by the acetate of lead were, after filtering, carefully washed with ether and dried. They were then severally decomposed by hydrochloric acid, and dissolved in hot alcohol. The acids thus obtained from the several lead-salts require to be again saponified and recovered by hydrochloric acid from aqueous solutions of the soap, as they contain traces of palmitic ether, owing to the use of alcoholic solutions in the

preparation. The first lead-salt yielded in this way an acid melting at 63° , the other an acid with a melting-point of 60° , which, however, was readily raised to 63° by one or two crystallisations.

These methods unite, then, in establishing the absence of any second solid fat-acid in the tallow. I will next prove the identity of the acid it does contain with palmitic acid.

Palmitic Acid.—The tallow is saponified with one-sixth of its weight of potash in alcoholic solution. When quite clear, water is added, and the alcohol distilled off. The solution of the soap is now added to very dilute sulphuric acid to separate the acids. The water from which the fat-acids have been separated contains free sulphuric acid, sulphate of potash, and glycerine; and this latter body may be readily separated from it by neutralising the free acid by carbonate of potash, evaporating off the water, and treating the residue with alcohol. The glycerine is recognised by its taste, and by the reaction which produces aceoleine. After frequently boiling on water the brown mass thus formed, it is pressed in a powerful press. The pressed mass is again melted, a little alcohol added to it, and after partial cooling the pressing force is repeated. After a few repetitions of this process, the mass becomes perfectly white, and its melting-point constant. Several crystallisations from a large amount of alcohol insure its purity, and the acid so formed has the properties of palmitic acid, as obtained by Frémy and others from palm oil. It is easily dissolved in hot alcohol, and separates from it, on cooling, in fine pearly scales. Very soluble in ether, it is but slightly so in cold alcohol. Its melting-point is $63^{\circ}5$, but it becomes hard at 63° . It reddens litmus when melted, as do also its solutions. The surface of the acid after melting and cooling is singular and characteristic, being formed in a series of irregular ridges of a circular form. It may be kept at a temperature of 250° to 300° for a length of time without alteration in melting-point or appearance. At a rather higher temperature, it distils over unchanged. A very slight discolouration, however, takes place in the retort, which is not imparted to the distilled acid. A slight residue in the retort, due probably to the formation of a trace of palmitone, has a melting-point of 72° . The distilled acid has the melting-point of the acid obtained from the alcoholic solution. Nearly pure specimens of the acid should alone be taken for distillation. Now, according to Schwartz,* the palmitic acid obtained from palm oil undergoes decomposition by distillation, its melting-point falling to 57° ; and, if this acid be kept at a temperature varying from 250° to 300° , it

* Ann. Ch. Pharm. ix. 58.

becomes converted into his palmitonic acid, which has a melting-point, according to him, of 51° , and has no crystalline structure.

Accordingly, the acid was prepared from palm oil by precisely the same process as that adopted to get the acid from the vegetable tallow. It was not quite so colourless, but had the same melting-point of $63^{\circ}\cdot 5$, and, like the acid from the Chinese tallow, it underwent no alteration from distillation beyond the same slight discoloured residue in the retort. Each acid was kept three-quarters of an hour, melted at a temperature between 260° and 280° , and both had the same melting-point of 63° ,—lower, by only half a degree, than the original melting-point of the acid. It is obvious, therefore, that palmitic acid does not undergo the changes thus ascribed to it. This acid is soluble in hot sulphuric acid, from which water reprecipitates it unchanged. Boiling it with nitric acid slowly changes it; but after treating it thus for an hour, and then melting with water, and finally dissolving in alcohol the solid yellow cake that floated on the cooled nitric acid, palmitic acid was obtained unchanged. The action, therefore, is a very gradual one. Palmitic acid loses nothing in weight at 100° . Dried at this temperature, and analysed by burning in some cases with chromate of lead, in others with oxide of copper and chlorate of potash, it yielded the following numbers :—

- I. 0·3260 grm. distilled acid gave :
0·8970 „ carbonic acid, and 0·3632 water.
- II. 0·3624 „ of acid separated from alcohol gave :
0·9955 „ carbonic acid, and 0·4030 water.
- III. 0·2872 „ of acid separated from alcohol gave :
0·7874 „ carbonic acid, and 0·3204 water.
- IV. 0·2930 „ of acid separated from alcohol gave :
0·8042 „ carbonic acid, and 0·3292 water.
- V. 0·3208 „ of acid separated from alcohol gave :
0·8790 „ carbonic acid, and 0·3607 water.

These numbers express the following percentage composition :—

	I.	II.	III.	IV.	V.	$C_{32}H_{52}O_4$ requires	Equiv.
Carbon ...	75·03	74·91	74·77	74·86	74·84	75·00	192
Hydrogen	12·39	12·36	12·40	12·49	12·55	12·50	32
Oxygen ..	12·58	12·73	12·83	12·65	12·61	12·50	32
	100·00	100·00	100·00	100·00	100·00	100·00	256

These numbers, then, agree with the formula of palmitic acid.

To determine the amount of water combined in the acid, it was melted with finely-powdered oxide of lead.

0.8513 grm. of the acid lost in this way 0.0310 of water.

	Required in Percentage.	Yielded by Experiment.
$C_{32}H_{31}O_3 = 247$	96.48	96.36
$H\ O = 9$	3.52	3.64
<hr/>	<hr/>	<hr/>
$C_{32}H_{32}O_4 = 256$	100.00	100.00

In order further to confirm the complete identity of the acid in Chinese vegetable tallow with palmitic acid as obtained from palm oil, many of its salts were prepared and analysed.

Palmitine; Palmitate of Lipylic Oxide.—To the melted tallow a mixture of alcohol and ether is added, and the mass powerfully pressed. The operation is repeated a great many times. The resulting mass is crystallised, first from its solution in mixed alcohol and ether, and subsequently from pure ether, till the melting-point is constant. The crystals from the last solvent are small, and of pearly lustre: in form, apparently, rhombic prisms. It does not crystallise after fusion, but forms a hard, wax-like, brittle, translucent mass. Insoluble, or nearly so, in cold ether and hot alcohol, it dissolves readily in boiling ether. Its reaction in fusion, as in solution, is neutral, while a strong heat decomposes it, with development of acroleine. When the melting-point is carefully taken, it shows a first melting-point at $50^{\circ}5$; after again solidifying, as the temperature is increased, it presents another melting-point at $66^{\circ}5$, its ultimate solidifying point being 49° . Its saponification yields an acid with the melting-point of palmitic acid.

The action of aqueous solution of potash on pure palmitine is extremely slow; in fact it is very difficult so to saponify it; and though the presence of oleine, by the solvent action of the oleine soaps, tends much to accelerate this saponification, it is possible to remove a very large part of the oleine by treatment with a limited supply of alkali. Thus palmitine may be obtained in a comparatively pure state from the tallow by boiling the latter with a very small quantity of potash, adding the potash gradually and with care. The hard white cake of palmitine always retains a little of the soap, but after several times being melted on, and boiled out by water, it can be freed from this, and obtained nearly absolutely pure by crystallisations from alcohol. This is perhaps the best way of preparing the palmitine. It is certainly the most expeditious one.

Burned with oxide of copper and chromate of potash,—

I. 0.2976 grm. yields 0.8284 carbonic acid, and 0.3262 water.

II. 0.3184 „ „ 0.8896 „ „ 0.3445 „

		Found.	
		I.	II.
$C_{35}=210$	Carbon .	76.04	76.19
$H_{33}=33$	Hydrogen .	12.16	12.03
$O_4=32$	Oxygen .	11.80	11.78
<hr/>		<hr/>	<hr/>
$C_3H_2O, C_{32}H_{31}O_3=275$		100.00	100.00

Palmitate of Soda.—The acid is boiled with a dilute solution of carbonate of soda. The jelly formed on cooling, after pressure in linen and drying in the water-bath, is dissolved in boiling absolute alcohol, the solution filtered, and a little water added to keep the alkaline carbonate in solution. The jelly formed on cooling, after being again pressed out and dried, is the pure soda-salt, soluble in water and in dilute alcohol, from which it crystallises in large pearly scales.

Easily melting to a clear liquid, it is decomposed by a comparatively low temperature.

The soda contained in the salt dried at 110° was determined,—

I. 1.1328 grm. gave 0.2890 of NaO, $SO_3=0.1265$ soda.
 II. 1.0074 „ „ 0.2564 „ „ $=0.1124$ „
 III. 0.6990 „ „ 0.1785 „ „ $=0.0782$ „

		Yielded by Experiment.		
		I.	II.	III.
For an equiv. of acid .	Required. 88.78	88.82	88.84	88.81
„ „ soda .	11.22	11.18	11.16	11.19
<hr/>		<hr/>	<hr/>	<hr/>
		100.00	100.00	100.00

Palmitate of Baryta.—A boiling alcoholic solution of palmitic acid is treated with ammonia in slight excess, and precipitated by an aqueous solution of acetate of baryta. The thick flocculent precipitate is washed with alcohol, containing at first some acetic acid to remove

* According to Berthelot's views of the composition of the natural fats, the formula of palmitine should be,—



that is to say, glycerine, in which 3 at. H are replaced by 3 at. of the oxygen-radical of palmitic acid, $C_{35}H_{31}O_2$. This formula requires 75.92 per cent. carbon and 12.16 hydrogen, numbers agreeing rather more closely with the author's analysis than those derived from the formula $C_{35}H_{73}O_4$ [or $C_{105}H_{99}O_{12}$]. Moreover, Stenhouse's analysis of palmitine obtained from palm-oil gives 75.6 per cent. C and 12.1 H. Berthelot has also prepared an artificial *tripalmitine*, agreeing in melting-point and other properties with natural palmitine. [Vide Ann. Ch. Phys. [3] xli. 240.—Ed.]

carbonate, and finally with water. It is a dull white powder, readily decomposed by heat.

- I. 0.7554 grm. yielded 0.2712 BaO, $\text{SO}_3 = 0.1783 \text{ BaO}$.
 II. 1.0391 " " 0.3736 " " = 0.2453 "
 III. 0.9800 " " 0.3530 " " = 0.2318 "

	Required.	Yielded by Experiment.		
		I.	II.	III.
For an equiv. of acid .	76.35	76.42	76.39	76.35
" " baryta .	23.65	23.58	23.61	23.65
	100.00	100.00	100.00	100.00

Palmitate of Magnesia.—The hot alcoholic solution of the acid, after treatment with ammonia and chloride of ammonium, is precipitated by acetate of magnesia. The fine white voluminous precipitate, after washing with alcohol, and subsequently with water, exhibits under a lens small four-sided leaf-like crystals. It can be fused to a clear liquid without decomposition.

- I. 0.6966 grm. yielded 0.0563 magnesia.
 II. 0.6140 " " 0.0490 "
 III. 0.7530 " " 0.0593 "

	Required.	Found.		
		I.	II.	III.
For an equiv. of acid . .	92.26	91.92	91.99	92.02
" " magnesia.	7.74	8.08	8.01	7.98
	100.00	100.00	100.00	100.00

Palmitate of Lead.—Formed by double decomposition of the alcoholic solution of the soda-soap with an aqueous solution of nitrate of lead. The fine white crystalline precipitate is washed thoroughly with alcohol, and then with water. It melts at 108° , and when solid forms an enamel-like white mass.

- I. 1.1762 grm. gave 0.3696 oxide of lead.
 II. 0.9228 " " 0.2907 " "
 III. 0.374 " burnt with chromate of lead, yielded:
 0.7381 " carbonic acid, and 0.2988 water.

	Requires.	Found.		
		I.	II.	III.
C_{32} . .	53.53	—	—	53.74
H_{31} . .	8.64	—	—	8.86
O_3 . .	6.69	—	—	—
PbO . .	31.14	31.43	31.50	—
	100.00			

Palmitate of Copper.—This salt, which is a clear, blue, voluminous powder, is formed by precipitation of the soda-salt by very dilute sulphate of copper. It may be melted with care without decomposition, and forms a green fluid, but heat readily breaks it up.

I. 0·8904 grm. gave 0·1260 CuO = 14·15 per cent.

II. 0·9686 „ „ 0·1356 „ = 14·00 „

The salt theoretically requires 13·85 per cent. of oxide.

Palmitate of Silver.—I have already mentioned that the formation and analysis of this salt originally led to a probable inference as to the nature of the acid contained in the tallow. The salt was prepared by precipitating the alcoholic solution of the ammonia-soap of the acid, by means of alcoholic solution of nitrate of silver, in the presence of an excess of ammonia. The analyses marked [I.] to [V.], are those referred to in the earlier part of this paper. The remainder of the analyses were performed with the silver-salt formed by the mutual decomposition of the soda-salt and nitrate of silver, in alcoholic solution. In both cases the salt formed is white, and nearly unchanged by light when dry.

[I.]	0·6715	grm. gave	0·2007	gr. =	29·89	per cent.	Ag =	32·11	per cent.	AgO.
[II.]	0·6700	„ „	0·2088	„ =	29·97	„ „	„	32·19	„ „	
[III.]	0·6711	„ „	0·2002	„ =	29·83	„ „	„	32·04	„ „	
[IV.]	0·6605	„ „	0·1970	„ =	29·83	„ „	„	32·04	„ „	
[V. (i.)]	0·5972	„ „	0·1790	„ =	29·97	„ „	„	32·19	„ „	
[V. (ii.)]	0·6395	„ „	0·1914	„ =	29·93	„ „	„	32·15	„ „	

Preparation from the soda-salt :—

VI.	0·8452	„ „	0·2476	„ —	„ „	„ =	31·46	„ „	
VII.	1·0076	„ „	0·2966	„ —	„ „	„ =	31·62	„ „	
VIII.	1·1062	„ „	0·3269	„ —	„ „	„ =	31·75	„ „	
Calculation requires				31·97	„ „	

The analyses of two of the salts made in the earlier part of the investigation, and of two of the salts made from the soda-soap by my assistant more recently, are subjoined :—

Of acid	[II.]	0·4635	grm. gave :	
		0·9006	„ carbonic acid, and	0·3545 water.
	[III.]	0·4725	„ gave :	
		0·9175	„ carbonic acid, and	0·3557 water.
	IX.	0·5167	„ recent preparation, gave :	
		1·0094	„ carbonic acid, and	0·3996 water.
	X.	0·4652	„ recent preparation, gave :	
		0·8996	„ carbonic acid, and	0·3645 water.

These analyses correspond as follows with the numbers required by calculation :—

	Required.	Found.			
		[II.]	[III.]	IX.	X.
Carbon . . .	52·88	52·99	52·95	53·28	52·73
Hydrogen . .	8·54	8·50	8·36	8·59	8·75
Oxygen . . .	6·61	6·32	6·65	—	—
Oxide of silver .	31·97	(32·19)	(32·04)	—	—
	<hr/> 100·00	<hr/> 100·00	<hr/> 100·00		

Palmitic Ether; Palmitate of Oxide of Ethyl.—Dry hydrochloric acid gas passed through a warm solution of palmitic acid in very strong alcohol, gives rise to the ether, which separates as an oily substance. It is purified by boiling with water, agitation with carbonate of soda, dissolving in alcohol, and finally precipitating it from this solution by water. It is a colourless, hard, brittle substance, with a slightly ethereal smell; melts at 25° , and, on solidifying, assumes a crystalline structure. It distils at a high temperature unchanged. Insoluble in water, it crystallises from an alcoholic solution in long, hard, prismatic needles. It is unchanged by dilute nitric acid, but immediately decomposed on heating it with potash.

Burnt with oxide of copper and chlorate of potash,—

I. 0·2345 grm. yielded 0·6542 carbonic acid, and 0·2704 water.

II. 0·2567 „ „ 0·7116 „ „ 0·2970 „

	Calculated.		Found.	
			I.	II.
For $C_{36} = 216$	76·06		76·08	75·65
$H_{36} = 36$	12·68		12·79	12·86
$O_4 = 32$	11·26		11·13	11·49
<hr/> $C_4H_5O, C_{32}H_{31}O_3 = 284$	<hr/> 100·00		<hr/> 100·00	<hr/> 100·00

For the preparation of the above salts, and for most of the analyses made of them, as well as for his skilful attention to the investigation, I am much indebted to my assistant, Dr. Ewald.

Palmitone.—This compound is formed by distilling palmitic acid with one-fourth of its weight of lime, and by several crystallisations of the distillate from alcohol.

It is a substance with a melting-point of 84° , and solidifying-point of 80° . This body, as it crystallises from alcohol, presents itself in white pearly scales; from fusion it solidifies in a pearly scaly mass, which is readily powdered, and is then highly electric. Neither dilute nitric acid nor potash act upon it. A mixture of nitric and sulphuric

acids at once blackens and destroys it. It is highly soluble in benzol. The palmitone was analysed, giving the following numbers:—

- I. 0.2987 grm. burnt with oxide of copper and chlorate of potash, gave:
 0.9035 „ carbonic acid, and 0.3700 water.
 II. 0.2954 „ gave 0.8968 carbonic acid, and 0.3727 water.

		Found.	
		I.	II.
C ₆₂ . .	372	82.49	82.80
H ₆₂ . .	62	13.76	14.02
O ₂ . .	16	3.75	3.18
	<hr/> 450	<hr/> 100.00	<hr/> 100.00

ANALYSIS OF THE VEGETABLE TALLOW ITSELF.

This analysis was originally made to ascertain whether any substance was present containing a higher percentage of carbon than palmitine or oleine. The tallow was dissolved in a large quantity of ether, and filtered. The ether was then distilled off, and the residue boiled out with water. The tallow was then thoroughly dried in a water-bath. While remaining fused in the water-bath, a few yellowish flocks separated, from which the tallow was poured off.

0.2621 tallow gave 0.7238 carbonic acid, and 0.278 water,	
corresponding to 75.31 per cent. of carbon,	
„ 11.79 „ hydrogen,	
„ 12.90 „ oxygen.	
	<hr/> 100.00

From this analysis we may fairly attempt a calculation of the constitution of the vegetable tallow. In fact, as

	Carbon.	Hydrogen.	Oxygen.
Oleine, by calculation, contains	70.8	11.3	17.9
And Palmitine	76.36	12.0	11.64

an elimination of two unknown quantities from two simple equations gives the proportion of palmitine to oleine as 4 eqivs. of the former to 1 of the latter.

The numbers thus obtained are—

	From the Calculation.	Found by Analysis.
Carbon	74.97	75.31
Hydrogen	11.80	11.79

For, out of the data here given we may construct two equations. Taking x for the number of equivalents of palmitine, and y for that of the oleine present in the tallow, and equating the carbon ratios of the three substances, as the least liable to error, we have—

$$76.36 x + 70.8 y = 75.31$$

$$\text{and} \quad x + y = 1$$

$$\text{whence eliminating } y, \quad x = \frac{75.31 - 70.8}{76.36 - 70.8} = \frac{4.51}{5.56} = .80 \text{ nearly}$$

$$\text{and} \quad y = 1 - x = .2 \text{ nearly}$$

$$\therefore \frac{x}{y} = \frac{4}{1}.$$

This is sufficient to prove that the numbers obtained by analysis of the tallow are compatible with, and, in fact, are explained with great simplicity by the view that this body contains only palmitine and oleine.

Nevertheless, it appeared interesting to ascertain that the oleic acid present in the tallow was of the ordinary formula, and my assistant, Dr. Ewald, undertook the investigation of it.

A portion of the tallow was saponified; the acids were then separated by hydrochloric acid, melted at a low temperature, mixed with alcohol, and cooled. The solidified mass was very strongly pressed; the fluid expressed was diluted with alcohol, quickly filtered, and precipitated by basic acetate of lead. The precipitate, after washing by alcohol and separation of the alcohol by pressure, was rapidly dried over sulphuric acid *in vacuo*. The dried and pulverised salt was then exhausted by cold ether, which takes up the oleate of lead only. The solution is decanted from the residue, and decomposed by dilute hydrochloric acid in a stoppered glass cylinder, without access of the air.

The chloride of lead rapidly subsides, leaving the clear yellow solution of oleic acid in the ether. This solution is now distilled from another flask by a gentle heat, in the water-bath, to separate the ether, and the residue dissolved in alcohol. From this solution the oleic acid is precipitated, by the addition of ammonia in slight excess and chloride of barium, as the pure oleate of baryta. It is quite white, settles quickly, and is filtered and washed with ether. This washing with ether, according to Heintz, at once protects the precipitate from the air, and dissolves a salt containing more baryta than the neutral oleate.

The salt so prepared is quickly pressed and dried *in vacuo*, and finally in an air-bath at 50° to 60°. It was burnt with oxide of copper and chlorate of potash.

I. 0.4678 grm. yielded 1.0636 carbonic acid (made up of 1.0342 in the potash apparatus + 0.0294 absorbed by the baryta to form 0.1317 of carbonate of baryta), and 0.4056 water.

II. 0.6364 grm. yielded 0.2122 BaO, $\text{SO}_3 = 0.1393$ BaO.

III. 0.6908 „ „ 0.2310 „ „ = 0.1517 „

		Found.			
		Calculated.	I.	II.	III.
C_{36} . .	216.0	61.79	61.80	—	—
H_{33} . .	33.0	9.44	9.64	—	—
O_3 . .	24.0	6.87	6.69	—	—
BaO .	76.5	21.90	21.87	21.79	21.96
	349.5	100.00	100.00	100.00	100.00

II.—On the Absorption of Chlorine in Water.

By HENRY E. ROSCOE, B.A., PH.D.

At the beginning of this century, Dalton and Henry set up the hypothesis, that the amounts of gas dissolved by a liquid vary as the pressure under which the absorption takes place. As, however, this relation between the absorbed gas and the pressure could not be deduced from Dalton and Henry's own experiments, and still less from the later ones of Saussure, it has been regarded by chemists as an ungrounded hypothesis, until Professor Bunsen,* in his late research, showed that it had a foundation in a true law.

A series of very careful experiments which Dr. Carius and Dr. Schönfeld have carried out with the absorptiometer described by Bunsen, not only give fresh proofs of the exactitude of the law, but show beyond doubt that it is applicable to gases of very great solubility.

It thus appears of great interest to examine the absorptiometrical relations of gases at the limits of the temperatures at which the same are capable of entering into chemical combination with the solvent. Dr. Schönfeld has examined sulphurous acid in this respect, and has found that the law is followed even at temperatures which ap-

* Phil. Mag., Feb. and March 1855; Ann. Ch. Pharm. xciii. 1.

proach the point where this acid forms a crystalline hydrate with the solvent.

In the following research I shall describe the absorptiometrical relation which exists between chlorine and water at temperatures approaching that at which hydrate of chlorine is formed. As the absorption-coefficient of this gas has already been accurately determined at Schönfeld, I have been able to confine myself to the examination of mixtures of gas of known composition containing chlorine.

The first mixture of gases examined was that evolved by the electrolysis of concentrated hydrochloric acid. The electrolysis was conducted in a small flask of about 100 cubic centimeters' capacity, filled with hydrochloric acid, into which two poles of conducting carbon dipped. A glass tube, with the upper end drawn out, was fastened on to the neck of the flask by means of a caoutchouc ring, and through the tube were melted two platinum wires, which communicated below with the carbon poles and above with the battery. The gas, obtained by a current of four of Bunsen's elements, was washed by passing through a series of bulbs containing water, blown on a glass tube and placed in an oblique position.

The composition of the gas thus obtained by electrolysis must first be determined. For this purpose the gas was dried over fused chloride of calcium, and led into a tube of known capacity, drawn out at both ends, until there could be no doubt that the last traces of atmospheric air were driven out. After accurate observation of the temperature and pressure, the tube filled with the mixture of gas was closed with the necessary precautionary measures, and one end opened under a solution of iodide of potassium; and in order to effect the rise of the liquid, this was done at a lower temperature than that at which the gas was collected. The iodide of potassium was immediately absorbed, and a quantity of iodine, equivalent to the free chlorine present, was separated out.

From this free iodine the amount of chlorine present in the tube was determined by Bunsen's volumetric method.* Two experiments with gas collected at separate occasions gave—

I.	II.
† $\alpha = 0.0024869$	$\alpha = 0.002443$
$t = 92.0$	$t = 67.0$
$t_1 = 59.9$	$t_1 = 58.3$
$n = 5.$	$n = 2.$

* Ann. Ch. Pharm. lxxxvi. 265; Chem. Soc. Qu. J. vi. 90.

† The signification of the various letters will be seen by reference to the original research.

From these numbers the volume of chlorine V reduced to 0° C. and 0.76 pressure of mercury contained in the tubes used in the experiments, is found in cubic centimeters by means of the formula—

$$(1) \quad \frac{\alpha (nt - t_1) \text{ Cl}}{0.0031823 \text{ l.}} = V$$

in which 0.0031823 is the weight in grms. of 1 cubic centimeter of chlorine at 0° C. and 0.76 pressure of mercury.

The first experiment gave 16.24; the second, 87.36 cub. cent. chlorine at 0° C. and 0.76 pressure of mercury.

If the total capacity of the tube be called C , the barometric pressure at the time of closing P , and the temperature during the same time T , the total volume of gas reduced to 0° C. and 0.76 contained in the tube is found by the following formula:—

$$(2) \quad \frac{C \cdot P}{(1 + 0.00366 T) 0.76} = V_1$$

For Experiments (1) and (2) the following values were found:—

	I.		II.
C . .	34.81	. . .	190.24
P . .	0 ^m .7415	. . .	0 ^m .7265
T . .	11 ^o .6 C.	. . .	11 ^o .1 C.

This gives the total volume of the first tube 32.58; of the second, 174.65. If, now, the respective volumes of chlorine found by graduation be subtracted from the total volumes, the volume of hydrogen gas present in the mixture will be obtained.

The composition of the two mixtures of gas was, therefore,—

	I.	II.	Calculated.
Chlorine . .	49.85	50.02	50.00
Hydrogen . .	50.15	49.98	50.00
	<hr/> 100.00	<hr/> 100.00	<hr/> 100.00

As the liquid subjected to electrolysis only contained hydrochloric acid and water, the products of decomposition formed could only contain chlorine, hydrogen, oxygen, or the oxides of chlorine or hydrogen. The absence of *free* oxygen can be safely inferred from the experiments just cited, for every volume of oxygen which is set free by the electrolysis of water is necessarily accompanied by *two* volumes of hydrogen, whilst chlorine and hydrogen are set free in equal volumes by the electrolysis of hydrochloric acid. If, therefore, water were decomposed in the above manner, the analysis would not

have shown equal volumes of chlorine and hydrogen, but an excess of the latter, which, as already stated, was not the case. For the same reason, peroxide of hydrogen cannot be formed in the decomposition, as the presence of this body would cause a still greater proportional excess of hydrogen.

It only remains, therefore, to be shown, that in the mixed gas no oxygen-compounds of chlorine are present. Let us in the first place, to take a particular case, examine if the gas could contain hypochlorous acid. 2 vols. of hypochlorous acid consist of 2 vols. of chlorine and 1 vol. of oxygen; 1 vol. of oxygen is equivalent to 2 vols. of chlorine, and sets free in the volumetric process exactly as much iodine as 2 vols. of chlorine. This process leaves it, therefore, quite undecided whether 4 vols. of chlorine or 2 vols. of hypochlorous acid were present; and further, because in the electrolytic decomposition of 4 vols. of hydrochloric acid, as in electrolytic formation of 2 vols. of hypochlorous acid, exactly the same amount, 4 vols., of hydrogen, must be set free, it is clear that the volumetric process will always show equal volumes of chlorine and hydrogen, whether the gas be rendered impure by the presence of hypochlorous acid or not. The question as to the presence of this latter gas is, however, easily answered, when a direct estimation of chlorine with solution of silver is made together with a volumetric determination. The silver determination shows only the amount of chlorine, and not the oxygen of the hypochlorous acid, and therefore may give only half as large an amount of chlorine as the volumetric process. The two following experiments show that the amount of chlorine found by the volumetric method agrees so exactly with that found by the silver determination, that the absence of hypochlorous acid may be certainly deduced. By similar reasoning, the absence of all other volatile oxides of chlorine can be proved.

Three tubes were filled with the gas as formerly described. The first was opened under iodide of potassium, and analysed by the volumetric process; the two others were opened under tolerably concentrated sulphurous acid, by means of which the whole of the chlorine was reduced to hydrochloric acid and precipitated in presence of excess of nitric acid as chloride of silver.

The elements for the first tube were—

$$\alpha = 0.0024869 \quad n = 2 \quad t_1 = 59.3 \quad t = 76.1$$

and

$$T = 14.7 \quad P = 0^m.7464 \quad C = 43.20$$

From these are obtained—

- I. Volume of chlorine at 0° C. and 0.76 found by
the volumetric process 20.290 cc.
II. Ditto ditto calculated 20.131 „

The elements for the second tube were—

- Weight of chloride of silver 0.3980
„ silver (with ash) 0.0031

and $T=14^{\circ}.7$ $P=0.7464$ $C=66.70$

From these are obtained—

- I. Reduced volume of chlorine found by silver
determination 31.26 cc.
II. Ditto ditto calculated 31.018 „

The elements for the third tube were—

- Weight of chloride of silver 0.3834
„ silver (in ash) 0.0024

and $T=14^{\circ}.07$ $P=0.7464$ $C=64.27$

From these are obtained—

- I. Reduced volume of chlorine found by silver
determination 30.034 cc.
II. Ditto ditto calculated 29.949 „

After all these experiments and considerations, it may be fairly concluded that the electrolytic gas really consists of a pure mixture of equal volumes of chlorine and hydrogen.

As the absorption-coefficients of chlorine and hydrogen for water are known, a simple volumetric determination of an aqueous solution, saturated at a particular temperature with the gaseous mixture, is all that is required to determine if chlorine obeys the law of absorption, and if so, up to what distance from the point at which hydrate of chlorine is formed. For if α represent the absorption-coefficient of chlorine, P the barometer pressure, v the volume of chlorine, and v_1 the volume of hydrogen contained in the mixed gas, which is passed through a volume h of water until it is saturated, the amount of chlorine V dissolved in the water must have the following value if the law of absorption is applicable:—

$$(3) \quad \frac{h \cdot \alpha \cdot Pv}{0.76 (v + v_1)} = V.$$

It will be as well to give here for reference the absorption-coefficients for chlorine and water (α) as found by Dr. Schönfeld:—

0° C.	Coefficient.	0° C.	Coefficient.	0° C.	Coefficient.
10. . . .	2.5852	21. . . .	2.1148	31. . . .	1.7104
11. . . .	2.5413	22. . . .	2.0734	32. . . .	1.6712
12. . . .	2.4977	23. . . .	2.0322	33. . . .	1.6322
13. . . .	2.4543	24. . . .	1.9912	34. . . .	1.5934
14. . . .	2.4111	25. . . .	1.9504	35. . . .	1.5550
15. . . .	2.3681	26. . . .	1.9099	36. . . .	1.5166
16. . . .	2.3253	27. . . .	1.8695	37. . . .	1.4785
17. . . .	2.2828	28. . . .	1.8295	38. . . .	1.4406
18. . . .	2.2405	29. . . .	1.7895	39. . . .	1.4029
19. . . .	2.1984	30. . . .	1.7499	40. . . .	1.3655
20. . . .	2.1565				

Three experiments,* made at different temperatures with the same volume (9.834 cc.) of saturated solution, gave the following results:—

(1)	(2)	(3)
$n = 2$	$n = 1$	$n = 1$
$t_1 = 48.9$	$t_1 = 10.0$	$t_1 = 5.5$
$t = 58.6$	$t = 67.6$	$t = 60.3$
$T = 14.4$	$T = 21.0$	$T = 25.0$
$\alpha = 0.0024430$		

Calculated
from formula (3).

Hence the vol. chlorine at 0° C. and 0.76 at 14.4 is	14.70	11.65
" " " " "	21.0	12.643
" " " " "	25.0	11.99
		9.36

These figures show that the amounts of chlorine found in the saturated solution differed considerably from the amount which should be contained therein according to the law of absorption.

Let us now proceed to the consideration of the causes which might possibly effect this increased absorption of chlorine. It has been already shown that the gas employed in the experiments did not contain any amount of oxides of chlorine which could possibly produce this greatly increased coefficient of absorption. It is, however, quite possible that chlorine should act towards water as it does towards so many bases, and a formation of hydrochloric acid and

* It is almost unnecessary to state, that all the experiments on mixtures of chlorine and hydrogen were conducted in a darkened room, a candle being the only light present.

oxide of chlorine take place. It is possible that the compounds thus formed were not present in the gaseous mixture, because they were retained in solution by the liquids with which they came in contact. Such a partial decomposition of the water by chlorine into hydrochloric and hypochlorous acids would most satisfactorily account for the above irregularities. This question may be easily settled by an experiment founded upon the law of absorption. If we suppose that when chlorine is dissolved in water, hydrochloric acid and any volatile oxide of chlorine is formed, it is easily seen that not only the volumetric process, but also a direct silver determination, must give exactly the same results as would be found if the liquid contained only free chlorine. A totally different result will, however, be obtained if any gas which obeys the law of absorption—as, for instance, carbonic acid—be passed into a saturated solution of chlorine in water. If merely chlorine be present, it will be driven out by a stream of carbonic acid, and replaced by this gas in the proportion of their relative absorption-coefficients.

If, on the contrary, hydrochloric acid and a volatile oxide of chlorine are present together with free chlorine, the chlorine and oxides of chlorine will be driven out in an amount different from that of the hydrochloric acid, which, when dissolved in a large quantity of water, is not volatile. Thus a relation between the components will be brought about, by which the volumetric and silver determinations cannot give like results, because the original relation by which the hydrochloric and hypochlorous acids are present in the proportion capable of forming chlorine and water, does not now exist.

The following experiment, in which a stream of carbonic acid was passed in the dark through a solution of chlorine freshly prepared without access of light, shows that after the current of gas had passed through for three hours, the amounts of chlorine obtained by volumetric and silver determinations agreed exactly. The gas was first passed into a bottle containing the chlorine solution, next into a second bottle containing distilled water, and the resulting solution in both bottles was examined.

ANALYSIS FROM THE FIRST BOTTLE.

Volumetric method—

$$\alpha = 0.0024869$$

$$(1) \quad n=2 \quad t_1=50.5 \quad t=72.0$$

$$(2) \quad n=2 \quad t_1=53.4 \quad t=71.0$$

Silver determination—

(1)	Chloride of silver	.	.	.	0·2617
	Silver	.	.	.	0·0010
(2)	Chloride of silver	.	.	.	0·2443
	Silver	.	.	.	0·0050

These elements give—

		(1)	(2)
Reduced volume of chlorine found by the			
volumetric method	.	20·421	19·962
Ditto ditto silver determination		20·517	19·599

ANALYSIS FROM THE SECOND BOTTLE.

Volumetric method—

$$\alpha = 0\cdot0024869$$

(1)	$n=2$	$t_1=46\cdot8$	$t=71\cdot9$
(2)	$n=2$	$t_1=48\cdot0$	$t=71\cdot7$

Silver determination—

(1)	Chloride of silver	.	.	.	0·2701
	Silver	.	.	.	0·0012
(2)	Chloride of silver	.	.	.	0·2594
	Silver	.	.	.	0·0005

These elements give—

		(1)	(2)
Reduced volume of chlorine found by the			
volumetric method	.	21·185	20·836
Ditto ditto silver determination		21·346	20·303

The supposition of a decomposition of water by chlorine to account for the observed phenomena is, therefore, likewise unfounded.

As an objection might be raised to this experiment, that the oxides of chlorine are not volatile enough to be carried over from their solution by a foreign gas, I have examined the action of carbonic acid on a mixture of oxides of chlorine. The mixture of all the various oxides of chlorine, which is obtained by heating chlorate of potash with concentrated sulphuric acid, was dissolved in water, and a known volume of the solution submitted to volumetric analysis; this volume was found to be equivalent to 50·3 burette divisions of normal iodine solution. A rapid stream of carbonic acid was then passed through the solution, which, after fifteen minutes, was again volumetrically analysed, and the same volume of solution was found to be equal to

24·0 divisions; after the current of gas had passed for thirty minutes more, the same volume corresponded to only 3·7 divisions. The rapidity with which the values of the volumetric determinations decreased with the amount of gas passed through, shows how easily the oxides of chlorine are expelled from their solutions by other gases, and hence the former objection is entirely removed.

A similar result is arrived at when the mixture of hydrogen and chlorine, after being washed, is allowed to saturate a volume of water. It is here also easy to show that no oxides of chlorine have passed over, for in the following experiment the same amount of chlorine was obtained by volumetric and by silver determination :—

Chlorine and hydrogen absorbed in 9·843 cc. of water at 38° and 0^m·7339 pressure :

Volumetric method—

$$\alpha = 0\cdot0024430$$

$$(1) \quad n = 1 \quad t_1 = 31\cdot8 \quad t = 72\cdot4$$

$$(2) \quad n = 1 \quad t_1 = 31\cdot9 \quad t = 72\cdot0$$

Silver determination—

$$(1) \quad \text{Chloride of silver} \quad . \quad . \quad . \quad 0\cdot1117$$

$$\text{Silver} \quad . \quad . \quad . \quad 0\cdot0016$$

$$(2) \quad \text{Chloride of silver} \quad . \quad . \quad . \quad 0\cdot1087$$

$$\text{Silver} \quad . \quad . \quad . \quad 0\cdot0048$$

Mean reduced volume of chlorine from volu-

metric method 8·700 cc.

Ditto ditto silver determination . 8·8966 „

In order that no possible cause may be left undetermined, I have examined the action of free hydrochloric acid upon the solution of chlorine. It was possible that the formation of hydrochloric acid from the hydrogen and chlorine might induce a larger absorption of chlorine, and thus the phenomena be explained. It was, however, found that the presence of hydrochloric acid lessened, instead of increasing, the absorption-coefficient of chlorine.

Water containing $\frac{1}{100}$ th of its bulk of concentrated hydrochloric acid was saturated with chlorine at 14° and 0^m·7366 pressure, and the absorption-coefficient calculated according to the formula,—

$$(4) \quad \frac{\alpha (nt - t_1) \text{ Cl } 0\cdot76}{0\cdot0031823 \cdot I. h.}$$

The experiment gave, when $h=9.834$ —

$$\begin{aligned} (1) \quad n=2 \quad t_1=62.1 \quad t=74.9 \\ (2) \quad n=2 \quad t_1=60.0 \quad t=73.9 \end{aligned} \quad \alpha=0.0024869$$

Hence the

$$\begin{aligned} \text{Coefficient obtained is} & \quad . \quad . \quad . \quad 1.9786 \\ \text{Coefficient for pure water} & \quad . \quad . \quad . \quad 2.3911 \end{aligned}$$

One assumption alone remains after all these experiments, namely, that near the temperature at which the formation of hydrate of chlorine begins, the atoms of chlorine exert an attraction on those of the other gas present, and on the water, similarly to the law of Mariotte at the point of condensation, and that thereby the accuracy of the law of absorption is lessened. In order to form an idea of the amount of this molecular disturbance, it is possible to calculate the volume of chlorine which, for any given temperature, does not obey the law of absorption. The equations for this calculation are obtained from the volumes of chlorine which are absorbed in water, firstly for pure chlorine, and secondly for a known mixture of this gas with hydrogen. Let V be the reduced volume of chlorine absorbed in h volumes of water when pure chlorine is used; V_1 the volume of chlorine dissolved in h_1 volumes of water when the mixed gas is used; v the amount of chlorine in the mixed gas; v_1 the volume of hydrogen in the latter; P the observed barometric pressure; y the reduced volume of chlorine obeying the law of absorption, which is contained in the unit of water; x the reduced volume of chlorine which, by reason of the molecular action, is supposed to be withdrawn from the law of absorption.

The following equations give the values of x and y :—

$$(5) \quad V=hy+hx$$

$$(6) \quad V_1=\frac{h_1y}{0.76} \frac{Pv}{(v+v_1)}+h_1x$$

or,

$$(7) \quad x=\frac{V}{h}-y$$

$$(8) \quad y=\frac{\frac{V}{h}-\frac{V_1}{h_1}}{1-\frac{Pv}{0.76(v+v_1)}}$$

By means of these formulæ, the values of x and y for various temperatures have been calculated from the following determinations :—

Chlorine and Hydrogen—

$$\alpha = 0.0024869 \quad h_1 = 9.834$$

I.	$T^\circ = 13^\circ.5$	$P = 0.7431$	$n = 2$	$t_1 = 39.2$	$t = 53.85$
II.	$T^\circ = 14^\circ.3$	$P = 0.7414$	$n = 2$	$t_1 = 48.9$	$t = 58.6$
III.	$T^\circ = 21^\circ.0$	$P = 0.7402$	$n = 1$	$t_1 = 10.0$	$t = 67.6$
IV.	$T^\circ = 25^\circ.0$	$P = 0.7431$	$n = 1$	$t_1 = 5.5$	$t = 60.3$
V.	$T^\circ = 30^\circ.0$	$P = 0.7320$	$n = 1$	$t_1 = 4.8$	$t = 53.2$
VI.	$T^\circ = 38^\circ.0$	$P = 0.7339$	$n = 1$	$t_1 = 31.85$	$t = 72.2$

Hence for—

$13^\circ.5$.	.	$y = 1.7831$	$x = 0.6496$
$14^\circ.3$.	.	$y = 1.7641$	$x = 0.6291$
$20^\circ.1$.	.	$y = 1.6721$	$x = 0.4880$
$21^\circ.0$.	.	$y = 1.6287$	$x = 0.4861$
$25^\circ.0$.	.	$y = 1.5984$	$x = 0.3589$
$30^\circ.0$.	.	$y = 1.3633$	$x = 0.3866$
$38^\circ.0$.	.	$y = 1.0625$	$x = 0.3771$

In order to determine whether the amount of this molecular disturbance was dependent upon the nature of the gas with which the chlorine is in contact, mixtures of known volumes of chlorine and carbonic acid were examined, and in a similar manner the values of x and y calculated from the experiments.

The great difficulty of mixing a known volume of chlorine with a known volume of another gas was overcome by the following simple arrangement:—A large glass tube of about 80 to 150 cubic centimetres' capacity was drawn out, the glass thickened at either end, and pieces of glass rod ground to fit air-tight into the apertures. The capacity of the tube was then accurately determined, and it was afterwards completely filled with carbonic acid and closed. The tube thus filled was opened under a saturated solution of chlorine freshly prepared in the dark, and a part of the carbonic acid driven out by the saturated solution. The tube containing the mixture of chlorine, water, and carbonic acid gas, was next well shaken in a water-bath of known temperature, and one of the stoppers partly opened to allow the excess of gas to escape. By means of this agitation, the statical equilibrium of absorption was established between the chlorine and carbonic acid dissolved in the water, and the chlorine and carbonic acid present in the free gas.

An effect of this process was an increased volume of free gas. This increased volume was allowed to escape, and thereby the original pressure obtained, and the agitation and other operations were repeated until no more gas was evolved, and the pressure remained

constant; or in other words, until the equilibrium ensued. The free and absorbed gas must be present in a proportion which may be calculated from the law of absorption. This proposition is found by the formulæ 1 and 2 used in the former case. The experiments were made in the following manner:—After the tube had been completely agitated, it was weighed in order to obtain the volume of water employed, and the amount of dissolved chlorine was determined by the volumetric method. The chlorine contained in the gas was also estimated in the same way, the tube being cooled with ether and opened under iodide of potassium. A deduction was also made for chlorine contained in the residual water, the volume of which was found by a second weighing after the volumetric examination of the water. By these observations, all the data for the calculation of x and y are given.

To obtain from a series of experiments the values of x and y , the same formulæ were used, viz.

$$y = \frac{\frac{V}{h} - \frac{V_1}{h_1}}{1 - \frac{Pv}{0.76(v+v_1)}}; \quad x = \frac{V}{h} - y$$

where $\frac{V}{h}$ is, as before, the volume of pure chlorine dissolved in the unit of water; $\frac{V_1}{h_1}$ the volume of chlorine dissolved in the unit of water from the mixed gases chlorine and carbonic acid, v the volume of chlorine in the gas, and v_1 the volume of carbonic acid.

Two experiments thus conducted with varying volumes of chlorine, carbonic acid, and water, at the same temperature, show very closely approximative results:—

EXPERIMENT I.

$$T=29^{\circ}.5 \quad P=0.7428$$

Capacity of tube = 82.62 cc.;

Weight of tube empty = 16.745;

Weight of tube, water, and gas = 33.005;

Volumetric analysis of the solution: $n=1$; $t_1=3.5$; $t=70.8$;

Weight of tube and residual water = 17.192;

Volumetric analysis of the gas: $n=2$; $t_1=44.8$; $t=64.8$.

From these elements we obtain—

$$V_1=15.098 \quad v=18.120 \quad h_1=16.265 \quad v+v_1=67.455$$

Hence,

$$y=1.141; \quad x=0.6287.$$

EXPERIMENT II.

$$T=29^{\circ}\cdot 5 \quad P=0\cdot 7514$$

Capacity of tube, and weight of tube empty, same as I.

Weight of tube and solution = $34\cdot 69$;

Volumetric analysis of the solution : $n=2$; $t_1=58\cdot 0$; $t=68\cdot 0$;

Weight of tube and residual HO = $17\cdot 160$;

Volumetric analysis of the gas : $n=2$; $t_1=43\cdot 0$; $t=68\cdot 1$.

From these elements we obtain—

$$V_1=17\cdot 455 \quad v=19\cdot 939 \quad h_1=17\cdot 945 \quad v+v_1=64\cdot 775$$

Hence,

$$y=1\cdot 1456 \quad x=0\cdot 6241.$$

The following table shows the values of x and y for various temperatures, as calculated from the experiments with chlorine and carbonic acid :—

$13^{\circ}\cdot 5$...	$y=1\cdot 7940$...	$x=0\cdot 5955$
$14^{\circ}\cdot 4$...	$y=1\cdot 7948$...	$x=0\cdot 5963$
$17^{\circ}\cdot 5$...	$y=1\cdot 7990$...	$x=0\cdot 4599$
$20^{\circ}\cdot 5$...	$y=1\cdot 4024$...	$x=0\cdot 7638$
$22^{\circ}\cdot 0$...	$y=1\cdot 3129$...	$x=0\cdot 7605$
$25^{\circ}\cdot 0$...	$y=1\cdot 2214$...	$x=0\cdot 7191$
$29^{\circ}\cdot 0$...	$y=1\cdot 1022$...	$x=0\cdot 6675$
$29^{\circ}\cdot 5$...	$y=1\cdot 1438$...	$x=0\cdot 6264$
$36^{\circ}\cdot 0$...	$y=0\cdot 8230$...	$x=0\cdot 6283$

Mean value of x for all the experiments, $0\cdot 6399$.

From these experiments it is clear that, for the same temperature, the amount of chlorine not obeying the law of absorption, varies with the nature of the other absorbed gas, and that the absorption-coefficient of chlorine is also altered by this circumstance. It is seen from the first table of the coefficients for chlorine and hydrogen, that the amount of chlorine present as not obeying the law, diminishes as the temperature increases from the point at which hydrate of chlorine is formed. In the determinations with carbonic acid and chlorine, on the other hand, this diminution is not seen at the temperature at which the experiments were made.

III.—*On the Preparation of the Metals of the Alkalies and Alkaline Earths by Electrolysis.*

By A. MATTHIESSEN, PH.D.

THE following research, carried out at the suggestion of Professor Bunsen, in his laboratory, upon the Electrolytic Decomposition of the Salts of the Alkalies and Alkaline Earths, seems to show that the statements given in the Handbooks concerning the preparation and properties of the metals of the alkaline earths are for the most part false. Indeed, it is more than probable that the metals calcium and strontium have never before been isolated; for all the experimenters who have supposed that they have prepared the metals, describe them as silver-white, whereas the globules of metal as large as a pea, which I have observed, have the colour and lustre of gold alloyed with silver. The preparation of barium, strontium, and calcium, presents many singular difficulties; for if galvanic currents of various intensities be passed through the fused chlorides of these metals, by means of two large carbon poles, as used by Bunsen for the preparation of magnesium,* a number of small flames are observed, not only at the negative, but also at the positive pole, whether at a high or low temperature. These small flames are occasioned by the metal in the form of a powder, burning, rising at the anode, and carried to the cathode by the current of chlorine evolved there. At the same time a small quantity of basic chloride is formed round the anode, which hinders the further passage of the current. No metallic globules are found on opening the cooled crucible, and only exceptionally does a part of the chloride evolve hydrogen on moistening with water. As the mass of chloride surrounding the negative pole had a strongly alkaline reaction, there can be no doubt that the diminution of the strength of the current was owing to the formation of lime. This is explained by the fact that the chlorides, when fused in a vessel composed of a silicate, soon become alkaline under the influence of atmospheric moisture.

Professor Bunsen, in his Electrolytic Researches, has shown that the density of the current is the chief condition under which the electricity is able to overcome the chemical affinities of different substances. It was very probable, therefore, that with a current of greater density the formation of the oxides would be prevented, as Bunsen found in the preparation of chromium in the moist way.† Experiment showed

* Bunsen on Magnesium (*Ann. Ch. Pharm.* lxxxii. 137).

† *Pogg. Ann.* xci. 619.

that this hypothesis was perfectly correct; for if an iron wire of the size of a needle be used instead of the large carbon negative pole, globules of potassium, sodium, calcium, strontium, &c. &c., are easily reduced; so that in future the preparation of these metals will be an easy experiment for the lecture-table. Although so easily reduced, it is difficult to obtain the metal in a coherent mass, and to separate it from the surrounding chloride. The reduced metal being specifically lighter than the fused salt, it rises to the surface and burns before it can be collected. If one attempts to collect the metallic globules by means of a bell-shaped vessel of glass, the metal reduces the silicon, which separates out in the form of a black powder, and prevents the metal fusing. I propose three methods for avoiding these difficulties,—Firstly, by using a platinum wire as negative pole: this, however, gives an impure metal, or rather an alloy with platinum, which, being specifically heavier than the fused chlorides, sinks to the bottom of the vessel, and is there found as a metallic ball. Secondly, by fusing together the chlorides of two metals mixed in equivalent proportions: these double chlorides melt at a temperature so low, that even potassium and sodium are not volatilised in the melted mass. If the heat is regulated in such a manner that a solid crust is formed on the top of the melted mass, only round the negative pole, a large quantity of metal is found on it after cooling the crucible. The third method consists in the separation of the metal on the immediate surface of the melted chlorides, by means of a pointed iron wire as pole, on to which the fused metal hangs: a thin film of melted chloride serves as a varnish to protect it from oxidation. It naturally depends on the metal to be obtained, which of the three methods is most applicable.

I shall now proceed to describe the preparation and properties of calcium. One method—which is, however, very uncertain, but which, if it succeeds, gives globules of calcium larger than peas—is the following:—A mixture of two equivalents of chloride of calcium and one of chloride of strontium with a small quantity of chloride of ammonium, is fused in a Hessian crucible; an iron cylinder, serving as positive pole, is placed in the melted mass; within the iron cylinder is then placed a small porous cell previously made red-hot, and afterwards filled with the same mixture fused in a porcelain crucible. A thin iron wire or fine carbon point serves as the negative pole in the porous cell. If the porous cell be filled with mixture from $\frac{1}{4}$ inch to 1 inch higher than the outer crucible, it is easy to regulate the fire so that a solid crust shall be formed in the inner cell, whilst the outer mass remains liquid. If a current from six of Bunsen's elements be allowed

to pass through the mixture thus arranged for half an hour to an hour, a large amount of reduced calcium is obtained. I have, however, only obtained the metal by this method once or twice in globules; in all the other experiments, the metal was reduced in the form of a powder, which was present in some parts of the mixture in such quantity that, upon being scraped with a knife, it showed the colour and lustre of gold alloyed with silver. Such pieces, when thrown in water, cause a violent evolution of hydrogen, and when pulverised under strong alcohol, which dissolves the chlorides, leave a metallic powder only slowly oxidable, which, when rubbed in an agate mortar, gives gold-coloured streaks. This method, on account of its uncertainty, cannot be recommended, and I therefore proceed to describe a more simple and safe one, by which calcium is obtained in small globules. The same mixture of salts is used, and melted in a small porcelain crucible, in which a carbon positive pole is placed, and a thin harpsichord wire (wound round a thicker one), dipping only under the surface of the melted salt, is connected with the zinc of the battery.

In order to obtain the beads of calcium which hang on to the fine wire, the negative pole must be withdrawn about every two to three minutes, along with the small crust which forms around it. The surest method, however, to obtain the metal, although in very small beads, is by placing a pointed iron wire merely so as to touch the surface of the liquid: the great heat evolved, owing to the resistance to the current, causes the reduced metal to fuse and drop off from the point of the iron wire, and the bead is recovered from the liquid by means of a small iron spatula.

The properties of metallic calcium are the following:—It is a light-yellow metal of the colour of gold alloyed with silver; on a freshly filed surface, the lustre somewhat decreases the yellow colour, which becomes more apparent if the light be reflected several times from two surfaces of calcium: a thin film of oxide produces the same effect. The hardness approaches that of gold, being from 2 to 3. It is particularly ductile, and may be cut, filed, or hammered out to plates having the thickness of the finest paper, a piece not larger than a mustard-seed having been flattened to the size of 10 to 15 square millimetres, showing only a few cracks at the border.

Concerning the specific gravity of calcium, I shall return to it shortly in my paper on strontium and barium. In dry air, the metal retains its colour and lustre for a few days only, but in presence of moisture the whole mass is slowly oxidised. Heated on platina foil over a spirit-lamp, it burns at a red heat with an excessively bright flash, about equal in intensity to the voltaic arc. Calcium is only slowly acted upon

by dry chlorine, but, when heated, burns in that gas with a most brilliant light, as also in iodine, bromine, oxygen, sulphur, &c. With phosphorus it combines without ignition, forming phosphide of calcium. Heated mercury dissolves it to a white amalgam. Water is rapidly decomposed by the metal, with evolution of great heat and hydrogen; diluted nitric, hydrochloric, and sulphuric acids cause a still more rapid decomposition, the first acid often causing ignition. Concentrated nitric acid, even when heated almost to boiling, does not attack the metal, the action not beginning till the liquid boils. By using water as the liquid element, calcium is negative to potassium and sodium, but positive to magnesium. Nevertheless, calcium is not reducible by potassium or sodium from its chloride. This is easily proved by the following experiment:—If 1 equivalent of chloride of sodium, and 2 equivalents of chloride of calcium, or equal equivalents of chlorides of calcium and potassium, be melted in a small porcelain crucible over a Berzelius spirit-lamp, owing to the easy fusibility of the mixtures, the metals potassium and sodium may be easily prepared by electrolysis when the following precautions are taken:—The heat must be so regulated that a solid crust forms on the surface around the negative carbon pole, whilst the mixture remains fused, allowing the free evolution of chlorine round the positive pole: by this means, after the decomposition has continued for about twenty minutes, and the cooled crucible has been opened under rock-oil, a large amount of potassium or sodium, almost chemically pure, is generally obtained. If the same experiment be repeated at a white heat in a charcoal fire, with an iron wire as negative pole, small globules of potassium or sodium are seen burning on the surface, which, when analysed, are found to be also almost chemically pure.

From these experiments it appears that the metal formerly obtained by the reduction of chloride of calcium with the alkaline metals, cannot be calcium, but was most probably a mixture of potassium or sodium with aluminium, silicon, &c.

IV.—*On a peculiar Efflorescence of the Chloride of Potassium.*

By ROBERT WARINGTON.

As the chloride of potassium is not usually classed among the efflorescent salts in any of the numerous systems or manuals of chemistry, the following observations may not be without interest to some of the members of the Chemical Society.

This subject was first brought under my notice, some few years since, by a gentleman in the establishment at the Apothecaries' Hall, who had been endeavouring at his own lodgings to manufacture artificial ultramarine, in the course of which he had attempted (I believe in a common stove) to fuse silica with carbonate of potash: the fusion, however, had evidently, from the appearance of the substance obtained, been imperfectly effected,—from the want, I presume, of sufficient heat; and the resulting mass had been afterwards treated with hydrochloric acid. Not having obtained the kind of material that had been anticipated, owing to the incomplete manner in which the operation had been conducted, the whole was set aside for some time, when attention was again attracted to it by the appearance of an efflorescent growth which had taken place in the mass, and which had ruptured it into fissures in various directions, these fissures being filled with bands of a fibrous saline growth, very similar in appearance to the well-known double sulphate of iron and alumina, or hair salt of the disintegrated alum shale of Hurlet and Campsie.

It was in this state when it was placed in my hands, and being anxious as a preliminary to ascertain to what extent this efflorescence would go on, it was placed in a shallow dish loosely covered with a small cone of paper, to keep off the dust, and set aside in a closet. Under these circumstances, the beautiful silky growth continued gradually to increase, until the crystals had reached a very considerable length, and presented an appearance very similar to the tufts of the cotton grass, or the long cellular filaments of the thistle down, projecting in all directions from the porous matrix of the partially hydrated silica. These filamentous crystals were readily soluble in distilled water, yielding a clear and perfectly neutral solution; and on submitting them to analysis, they proved to be entirely composed of chloride of potassium.

Thus: 2 grs. of these effloresced filaments were dissolved in water, and the solution evaporated to dryness, to ascertain that no trace of silica was present, redissolved in water acidulated by nitric acid, and precipitated by a solution of nitrate of silver: this precipitate, collected and well washed, weighed, after drying, 3.78 grs. of chloride of silver.

The filtered solution and washings were then treated with hydrochloric acid to throw down the excess of silver salt, which precipitate was separated by a filter, and the clear liquor evaporated to dryness to decompose all the nitrates. The dry salt was next redissolved in water, a little hydrochloric acid added, and then precipitated by a solution of bichloride of platinum in excess, and the whole again

evaporated carefully to dryness. The crystalline product was then washed with ether-alcohol to remove all excess of the test, and the double chloride of platinum and potassium thus obtained dried: it weighed 6·4 grs. We have, therefore:—

Chloride of silver 3·78 = 0·932 chlorine.
 Chloride of platinum and potassium . 6·40 = 1·028 potassium.

1·960

Or,

Theory.
0·9491
1·0509
<hr/>
2·0000

When this efflorescent salt is submitted to examination by the microscope, it presents many very interesting phenomena: each apparently single thread is then found to be built up, as it were, of an aggregation of smaller filaments, intimately united together, and, as I shall presently show, having a cubic structure.

Viewed by a high magnifying power, a very curious appearance is exhibited. The single filaments are seen to be dotted along their whole length with slight depressions, and these depressions are found to be perfectly equidistant the one from the other over certain given lengths; thus, they are most widely separated at the lower part of the thread, or its base, and become more approximated, for certain intervals of distance, as the fibre elongates and gradually becomes smaller in its transverse dimensions. This phenomenon, I am induced to believe, indicates the step or point at which the growth of each individual crystal has originated, and therefore marks its point of attachment with the one previously formed, so that the filament ultimately resulting may be considered as a series of microscopically minute cubic crystals growing one upon the other continuously, and that the intervals of distance by which these depressions are separated from each other will indicate the diameter of the single cubic needle at that particular spot. These intervals of distance, measured by a micrometer in the field of the microscope, were found to range from $\frac{1}{10000}$ th to $\frac{1}{30000}$ th of an inch.

Again, when these filaments are fractured, they present a cleavage plane at right angles to the length of the fibre. They also prove to be single refractors, or equiaxial crystals,—that is, when viewed by polarised light in the field of the microscope, placed between the polarising and analysing plates or prisms, they exhibit no depolarising

power, nor allow the least ray of light to pass through them in the dark field, thus again confirming their structure as being cubical. I may mention here, also, that Gmelin, in his excellent "Manual of Chemistry," observes that the chloride of potassium frequently crystallises from its solutions in cubes prismatically elongated.

This appears, then, to be another instance of the peculiar crystalline growth, under the same cubic form, which sometimes occurs in solutions of the iodide of potassium, and a memorandum of which I laid before the Society on the evening of May 3, 1852.*

The remaining point which presented itself to my attention was to ascertain in what manner I could best preserve this beautiful efflorescent growth permanently, so as at the same time to admit of its transport without injury to the delicate silky fibres, which I had found were liable to fracture by the slightest touch. After some preliminary trials, I at last adopted the plan exhibited in the specimen before you, in which a thick cream of plaster of Paris and water was first carefully introduced into the interior of the specimen jar, so as to cover the bottom to the depth of about half an inch, without soiling the sides; and while this was still in its semi-fluid state, the mass of silica, with its impregnating saline matter, was carefully imbedded in it, and the vessel, being loosely covered, was set aside. I should state also, that the crop of the efflorescent salt which existed on the surface of the mass was first moistened with water, in order that it might be dissolved and reabsorbed by the porous matrix before being cemented in the bottom of the jar. After a short time the efflorescence gradually commenced anew, the crystals slowly rising in tufts of beautiful silky fibres, and filling the whole of the lower part of the jar, until the filaments had many of them reached the length of from four to five inches.

V.—*On the Thermo-Electrical Currents generated in Elements where Bismuth is used to form the Joint.*

By RICHARD ADIE, Liverpool.

THE use of bismuth as a solder for thermo-electrical couples appeared to me to be worthy of trial for a variety of metals, in order to show the extent to which the action of couples might be governed by the nature of their joint. The arrangement of the bars and wires of me-

* Chem. Soc. Qu. J. v. 136.

tals to be tested, was to solder them together by means of small pieces of bismuth, and to form the other extremities of the bars into a circuit with a galvanometer. To each pair under examination, heat was applied, first on the right hand side, and then on the left hand side of the joint, when the effect on the direction of the thermo-electric current generated was observed by the galvanometer. After this manner, 72 thermo-electric couples were examined. The following is a summary of the effects observed.

In nine metals, when two bars of the same metal were joined by bismuth solderings, the positive electrical current flowed in an opposite direction to that of the heat current. These metals were gold, silver, platinum, copper, zinc, cadmium, antimony, iron, and soft steel.

In three metals used singly with bismuth solderings, the direction in which the heat crossed the joint, and that of the electricity, were the same. These metals were palladium, lead, and tin. Twenty-eight pairs of different elements soldered by bismuth, being combinations of the metals tested singly, showed the direction in which the heat crossed the joint to be opposite to that of the electricity, as in the case of the nine single metals tested,—total, thirty-seven pairs.

One pair of different metals soldered by bismuth showed heat and electricity to cross the joint in the same direction, as in the instance of the three single metals tested.

Thirty-one pairs of different metals soldered by bismuth showed the direction of the passage of the heat across the joint not to govern the electrical current; they acted according to their ascertained thermo-electrical relation, independently of the side of the joint on which the heat was applied.

On looking over these results, I was led to examine the instances of the three single and one double pair of elements, to see why they differed from the thirty-seven other cases, where the direction of the electrical current was governed by the passage of the heat across the joint. Their peculiarity appeared to me to arise from the tendency the bismuth had to alloy with these metals, and thus form joints of a mixture of metals, which gave them an indefinite character. I consequently sought to arrange these four cases with bismuth joints of a definite kind.

EXPERIMENT I.—Two slips of palladium were soldered together with a thin film of bismuth for the joint; their other extremities were connected with a galvanometer. When heat was applied, the passage of the heat and electricity across the joint was in the same direction, as I had previously noted. The soldered joint was broken asunder;

the palladium surfaces cleaned free from the bismuth solder; and to form a joint, a thin piece of bismuth was placed between the two slips of metal, and secured in its position by firm tying: by this means a couple was obtained where the bismuth had a definite surface. When heat was applied, first on the right and then on the left hand side of the joint, *the heat and electricity crossed it on opposite directions*, in the same manner as they had done in the thirty-seven cases where the direction of the electrical current was governed by a bismuth-soldered joint.

EXPERIMENT II.—Two pieces of lead-wire were formed into a couple with a small piece of bismuth tied firmly between them. In this case the passage of the heat and electricity across the joint was in opposite directions.

EXPERIMENT III.—Two pieces of tin-wire gave a result similar to No. II.

EXPERIMENT IV.—A wire of lead and a wire of tin, with a piece of bismuth tied between them for a joint, gave a similar result to Nos. I., II., and III.

These four experiments comprise the cases noted in the summary, where the passage of the heat and electricity across the joint was in the same direction; they now show the heat and electricity to cross the joint in opposite directions,—a change which has been effected by avoiding the mixture which soldering of these metals would produce.

To obtain pieces of bismuth for inserting in the joints for the above experiments, the point of a bar of that metal was held in the flame of a candle until large tear-like drops fell from it: these were received on a smooth surface below, in the form of thin circular discs. The discs admitted of being cut into small pieces. The weight of bismuth put in the joints for the above experiments varied from $\frac{1}{40}$ th to $\frac{1}{50}$ th of a grain; yet this small quantity of bismuth sufficed to render active pieces of lead and tin, which, without the bismuth joint, would only afford a trace of a thermo-electrical current.

The general result proved by these experiments is, *that the source of the thermo-electrical current is the surface of a joint*,—a fact which gives additional value to an observation I made, and which was published in the Edinburgh Philosophical Magazine for 1843, that a pair of bismuth and antimony bars soldered together by pure bismuth, and long employed to generate a powerful thermo-electric current, produced a disintegration of the bismuth at its surface of contact with the antimony.

VI.—*On Thermo-Electric Joints formed with the metals Antimony, Bismuth, and Palladium.*

By RICHARD ADIE, Liverpool.

EXPERIMENT I.—A bar of antimony 8 inches long was broken in the centre, and soldered together again with pure bismuth; while the solder was fluid, the two pieces of antimony were pressed firmly together, so that the coating of bismuth in the joint should be as thin as possible. When the right side of the joint was heated, the left became the positive thermo-electric element; and when the left side was heated, the right side stood positive. This effect, where the bismuth has no sensible thickness, is the same as if a long bar of that metal had intervened between the two pieces of antimony.

EXPERIMENT II.—A slip of palladium cut into two, had a bismuth joint prepared as thin as possible, like the experiment No. I. When the right side of the joint was heated, the left in this case became negative; and when the left side was heated, the right became negative.

EXPERIMENT III.—The same two pieces of palladium as in the last experiment, with a bismuth joint one-tenth of an inch in thickness. When heat was applied on the right side of the joint, the left side was positive, the result showing that the increase in the thickness of the bismuth joint had rendered the effect similar to that which would have been produced by a long bar.

EXPERIMENT IV.—A slip of palladium and a bar of antimony formed the couple for this experiment, joined together by a thin bismuth joint. The recognised action of these metals, when heated together, is that palladium becomes positive. When heat was applied to the antimony side, palladium was positive; and when heat was applied to the palladium, antimony stood positive for fifteen seconds; but as the heat penetrated through the joint, the palladium assumed the positive position, which it retained. The result of this experiment I consider as valuable, for illustrating the action of the first and second surface of a joint; for when the heat is applied to the palladium, we have for a short space the first surface in action, with antimony positive, then a reversal of the current when the heat reaches the second surface.

EXPERIMENT V.—A bar of antimony was tied firmly down to a bar of bismuth, with a small scale of sulphuret of silver inserted between them for a joint. When the antimony was heated to near 400°,

an attached galvanometer indicated the passage of a feeble current with the bismuth positive, or in its natural thermo-electric position; and when the heat was applied to the bismuth bar near the joint, the galvanometer showed bismuth the negative metal, with a feeble current passing. This experiment is not so satisfactory as the one with a sulphuretted silver wire connected with the bismuth, being more liable to fail from the couple becoming active at too low a temperature, or from the temperature required approaching near the melting-point of bismuth; but it has the advantage of exhibiting the two most opposite thermo-electric elements in an inverted position.

My object in giving the results of these experiments is to show cases where a thin coating of bismuth in a joint acts in several ways.

1st. The same as if it had been a bar of that metal in Experiment I. Instances of this kind are numerous among thermo-electric couples where the antagonistic negative and positive properties of the two elements are not strongly marked, as in the single metals, in zinc and silver, in gold and in many of its combinations, copper, &c.

2nd. Where a thin bismuth joint did not act as if it were a bar, and yet the direction of the flow of heat across the joint governed that of the electrical current generated. Cases of this kind are rare. With lead and tin I have met with very feeble currents of a like character, but the arrangement given is the most certain form of the experiment.

3rd. Where a thin bismuth joint acted for a brief period of time, as if it had been a long bar, and then acted like a couple in its recognised thermo-electric position, independent of the method of applying the heat. I have noticed this property in other thermo-electric couples, where palladium formed one of the elements.

The permanent action of the joint, after a lapse of fifteen seconds, where the recognised thermo-electric relation of the elements is maintained, notwithstanding the thin bismuth joint or the direction in which the heat is made to cross it, is one of frequent occurrence: we meet it in the combination of metals which have decided antagonistic thermo-electric positions, such as palladium, platinum, zinc, iron, antimony, &c.; but Experiment V. shows that such elements may have their natural thermo-electric position inverted by a joint offering greater resistance.

PROCEEDINGS
AT THE
MEETINGS OF THE CHEMICAL SOCIETY.

January 15, 1855.

Dr. A. W. WILLIAMSON, Vice-President, in the Chair.

The following gentlemen were introduced and admitted Fellows of the Society :—

Nevil Story Maskelyne, Esq., M.A., Oxford.
H. J. Smith, Esq., B.A., Oxford.
Charles Loudon Bloxam, Esq., King's College, London.
Charles W. Heaton, Esq., 26, Lime Street.
Fletcher Norton, Esq., 5, Stanhope Street, Hampstead Road.

The following donations were announced :—

"The Journal of the Society of Arts :—" from the Society.
"The Pharmaceutical Journal :—" from the Editor.
"Report of the Art-Union of London :—" from the Society.
"The Art-Union Almanack :—" from the Society.

The following gentlemen were duly elected Fellows of the Society :—

Matthew Warton Johnson, Esq.
Charles Tookey, Esq., 3, Mytre Street, Claremont Square.

The following papers were read :—

“On Thermo-Electric Joints formed with the metals Antimony, Bismuth, and Palladium :” by Richard Adie, of Liverpool.

“Investigation of the Vegetable Tallow from a Chinese Plant, the ‘*Stillingia sebifera*’ :” by Nevil Story Maskelyne, M.A., F.G.S.

“On the Absorption of Chlorine in Water :” by H. E. Roscoe, B.A., Ph.D.

February 5, 1855.

Dr. H. BENCE JONES, Vice-President, in the Chair.

The following donations were announced :—

“The Literary Gazette :” from the Publishers.

“The Journal of the Photographic Society :” from the Society.

“The Pharmaceutical Journal :” from the Editor.

“The Transactions of the Royal Scottish Society of Arts, Vol. IV. :” from the Society.

“Transactions of the Royal Society of Edinburgh, Vol. XXI. Part 1, for 1853 and 1854 :” and

“Proceedings of the Royal Society of Edinburgh, 1853 and 1854 :” from the Royal Society of Edinburgh.

“Transactions of the Royal Society of London for 1851, 1852, 1853, and part of 1854 :” from the Royal Society.

“List of the Council and Fellows, &c. of the Royal Society, Nov. 30, 1853 :” from the Royal Society.

“Illustrated Catalogue of the Calculi and other Animal Concretions contained in the Museum of the Royal College of Surgeons, Parts 1 and 2 :” from the Royal College of Surgeons.

“An Account of the Organic Chemical Constituents or Intermediate Principles of the Excrements of Man and Animals in the healthy state ; by W. Marcet, M.D. :” from the Author.

“The Journal of the Franklin Institute for November and December, 1854 :” from the Institute.

“Sitzungsberichte der kaiserlichen Akademie der Wissenschaften, mathematisch-naturwissenschaftliche Classe,” Band 12, Heft 5 ; Band 13, Heft 1 and 2.

“Register zu den ersten 10 Bänden der Sitzungsberichte geognostische Karte der Umgebungen von Krems und von Manhardsberge.”

"Jahrbuch der kaiserlich-königlichen geologischen Reichsanstalt," 1854: No. 2, April, May, June, Wien.

"Jahrbücher der kaiserlich-königlichen Central-Anstalt für Meteorologie und Magnetismus, von Karl Kreil, Wien:" Band 1, 1848 and 1849; Band 2, 1850.

"Ueber die Nicht-einfachheit der Metalle, des Schwefels, der Köhle, des Chlors, von Kotikovsky, Wien."

"Ofversigt af Kongl Vetenskaps Akademiens forhandlingar; Tionde Årgangen 1853, Stockholme."

"Bulletin de la Société Vaudoise des Sciences Naturelles:" Tome 3, Bulletin 30; Tome 4, Bulletin 32.

The following gentlemen were duly elected Associates of the Society:—

Frederick Stohmann, University College.

Frederick Versmann, University College.

The following papers were read:—

"On a peculiar Efflorescence of Chloride of Potassium:" by Robert Warington.

"On the Preparation of the Metals of the Alkalies and Alkaline Earths by Electrolysis:" by A. Matthiessen, Ph.D.

February 19, 1855.

Dr. A. W. WILLIAMSON, Vice-President, in the Chair.

The following donations were announced:—

"The Literary Gazette:" from the Publishers.

"The Journal of the Society of Arts:" from the Society.

"The Edinburgh Medical and Surgical Journal:" from the Publishers.

"The Journal of the Franklin Institute:" from the Institute.

"The American Journal of Science and Arts:" from the Editors.

A paper was read:—

"On the Thermo-Electrical Currents generated in Elements where Bismuth is used to form the Joint:" by Richard Adie, of Liverpool.

March 5, 1855.

COLONEL PHILIP YORKE, President, in the Chair.

The following donations were announced :—

“The Literary Gazette :” from the Publishers.

“The Journal of the Society of Arts :” from the Society.

“The Journal of the Photographic Society :” from the Society.

“The Pharmaceutical Journal :” from the Editor.

“The Quarterly Journal of the Geological Society :” from the Society.

“The Journal of the Franklin Institute :” from the Institute.

Mr. John Jones Bancroft, of Ruthen, North Wales, was duly elected a Fellow of the Society.

Dr. W. Odling made a verbal communication on “Chemical Notation.”

March 19, 1855.

Dr. G. D. LONGSTAFF, Vice-President, in the Chair.

The following donations were announced :—

“The Literary Gazette :” from the Publishers.

“The Journal of the Society of Arts :” from the Society.

“The Journal of the Photographic Society :” from the Society.

Dr. W. A. Miller delivered a discourse upon the “Action of Water on Lead.”

March 30, 1855.

Dr. A. W. WILLIAMSON, Vice-President, in the Chair.

The Report of the Council, and the Audited Account of the Treasurer, were read.

Mr. E. W. Brayley and Dr. W. Odling having been appointed Scrutators, the meeting proceeded to the election of Council and Officers for the ensuing year, and the following gentlemen were declared to have been duly elected :—

PRESIDENT.

W. A. Miller, M.D., F.R.S.

VICE-PRESIDENTS

(WHO HAVE FILLED THE OFFICE OF PRESIDENT.)

W. T. Brande, F.R.S.

Thomas Graham, F.R.S.

C. G. B. Daubeny, M.D., F.R.S.

Colonel Philip Yorke, F.R.S.

VICE-PRESIDENTS.

Warren De la Rue, Ph.D., F.R.S.

G. D. Longstaff, M.D.

H. Bence Jones, M.D., F.R.S.

A. W. Williamson, Ph.D.

SECRETARIES.

B. C. Brodie, F.R.S.

Theophilus Redwood, Ph.D.

FOREIGN SECRETARY.

A. W. Hofmann, Ph.D., F.R.S.

TREASURER.

Robert Porrett, F.R.S.

OTHER MEMBERS OF THE COUNCIL.

Thomas Anderson, M.D.

Charles Heisch, Esq.

G. B. Buckton, F.L.S.

Hugh Lee Pattinson, F.R.S.

Dugald Campbell, Esq.

John Stenhouse, LL.D., F.R.S.

J. H. Gladstone, Ph.D., F.R.S.

R. D. Thomson, M.D., F.R.S.

W. C. Henry, M.D., F.R.S.

Robert Warington, Esq.

William Herapath, Esq.

John Thomas Way, Esq.

The thanks of the meeting were voted to the President, Officers, and Council for their services during the past year.

NOTICES
OF
PAPERS CONTAINED IN OTHER JOURNALS.
BY HENRY WATTS, B.A., F.C.S.

On Osmotic Force.*

By Thomas Graham, F.R.S., &c.

THE expression "Osmotic Force" (from *ὥσμος*, *impulsio*) has reference to the endosmose and exosmose of Dutrochet.

The force of liquid diffusibility will still act if we interpose between the two liquids a porous sheet of animal membrane or of unglazed earthenware; for the pores of such a septum are occupied by water, and we continue to have an uninterrupted liquid communication between the water on one side of the septum and the saline solution on the other side.

To impel by pressure any liquid through the pores of such a septum may be extremely difficult, from the interference of frictional resistance and the attraction of capillarity. But these last forces act on masses and not on molecules, and the ultimate particles of water and salt which alone diffuse, appear really to permeate the channels of the porous septum with little or no impediment. A comparative experiment on diffusion, with and without septa, is easily made by means of a wide-mouthed phial, which is filled completely with saline solution and then immersed in water, in one experiment with the mouth of the phial open, and in the other experiment with the mouth covered by membrane. In a fixed time, such as seven days, a certain quantity of salt leaves the phial by diffusion. This quantity was reduced to one-half when the strong and thick membrane of the ox-gullet was used to cover the mouth of the phial; and it was not affected in a sensible degree by passing through a thinner membrane, consisting of ox-bladder with the outer muscular coat removed. In the last experiment the actual diffusates were 0.631 grm. common salt in the absence of the membrane, and 0.636 grm. common salt with the membrane interposed, which may be considered as the same quantity. The diffusion of a salt appears to take place, therefore, without difficulty or loss through the substance of a thin membrane, although the mechanical flow of a liquid may be nearly stopped by such an obstacle.

It is well to bear in mind the last fact in the consideration of what

* Phil. Trans. 1854, 177.

is seen in an endosmotic experiment. An open glass tube, with one end expanded into a bell form and covered by tight membrane, forms a vessel which may be filled with a saline solution and immersed in a jar of pure water. The volume of liquid in this osmometer soon begins to increase and is observed to rise in the tube, while the simultaneous appearance of salt in the water of the jar may easily be verified. M. Dutrochet described the result as the movement of two unequal streams through the membrane in opposite directions, the smaller stream being that of the saline solution flowing outwards, and the larger that of pure water flowing inwards. The double current has been always puzzling, but the expression of the fact becomes more conceivable when we say (as we may do truly) that the molecules of the salt travel outwards by diffusion through the porous membrane. It is not the whole saline liquid which moves outwards, but merely the molecules of salt, their water of solution being passive. The inward current of water, on the other hand, appears to be a true sensible stream or a current carrying masses. The passage outwards of the salt is inevitable, and being fully accounted for by diffusibility, requires no further explanation. It is the water current which requires consideration, and for which a cause must be found. This flow of water through the membrane I shall speak of as osmose, and the unknown power producing it as the osmotic force. It is a force of great intensity, capable of supporting a column of water many feet in height, as shown in Dutrochet's well-known experiments, and to which naturalists are generally disposed to ascribe a wide sphere of action, both in the vegetable and animal kingdoms.

Cannot liquid diffusion itself, it may first be asked, contribute to produce osmose? Diffusion is always a double phenomenon, and while molecules of salt pass in one direction through the membrane, molecules of water no doubt pass by diffusion in the opposite direction at the same time, and replace the saline molecules in the osmometer. Water also is probably a liquid of a high degree of diffusibility; at least it appears to diffuse four times more rapidly than alcohol, and four or six times more rapidly, therefore, than the less diffusive salts. A possible consequence of such inequality of diffusion is, that while one grain of a certain salt diffuses out of the osmometer, four or six grains of water may diffuse into the osmometer. Liquid diffusion, I believe, generally tends to increase the volume of liquid in the osmometer, and a portion, if not the whole, of the small osmose of chloride of sodium, sulphate of magnesia, alcohol, sugar, and many other organic substances, may be due to the relatively low diffusibility of such liquefied bodies compared with the diffusibility of water. But many substances, it will immediately appear, are replaced in experiments of endosmose, not by four or six, but by several hundred times their volume of water, and manifestly some other force besides diffusion is at work in the osmometer.

An explanation of osmose has been looked for in capillarity by Poisson, Magnus, and by Dutrochet himself. Combining diffusion with this idea, we might imagine that the pure water which first occupies the pores of the septum suffers a sudden and great loss of its capillarity-force when the salt of the osmometer enters the pores by diffusion and mixes with the water they contain. Experiments published by Dutrochet give a capillary ascension to pure water of 12 millimeters, and to a solution of common salt, of density 1·12, 6·14 millimeters, or only one-half of the former ascension. If a porous septum, occupied by such a saline solution, had the same solution in contact with one surface, and pure water in contact with the other surface (the actual condition of the septum in an osmotic experiment), the pure water should enter its pores from its high capillary attraction, and, like a solid piston, force out the saline solution from them: the saline solution so displaced would go to swell the liquid within the osmometer. When the pure water, now again occupying the pores, came in time to acquire salt by diffusion, the displacement would be repeated, and a continuous osmose or flow of water inwards be in fact established.

This explanation is attended with certain physical difficulties, but it is unnecessary to discuss these, as the experimental basis of the hypothesis is unsound. The great inequality of capillarity assumed among aqueous fluids does not exist. Many saline solutions which give rise to the highest osmose are, I find, undistinguishable in capillarity from pure water itself. To obtain constant results with saline solutions, the capillary tube must be retained for some minutes in the saline solution at a boiling temperature, and afterwards be cooled without removal from the liquid, otherwise the indications are singularly irregular and most fallacious.

The near equality in capillarity of solutions of the most different composition is very apparent in my observations, which are placed together in the following series of capillary ascensions:—

Capillary ascension of several liquids in the same glass tube.

	Millimeters.
Water, at 58° F.	17·75
Water, at 66°	17·55
Carbonate of potash, 0·25 per cent., in water, at 63°	17·2
Carbonate of potash, 10 per cent., in water, at 66°.	17·55
Carbonate of soda, 1 per cent., at 61°	17·55
Carbonate of soda, 10 per cent., at 55°	16·85
Sulphate of potash, 1 per cent., at 58°	17·15
Sulphate of potash, saturated solution, at 58°	16·3
Sulphate of soda, 1 per cent., at 55°	17·75
Sulphate of soda, 10 per cent., at 58°	16·95
Hydrochloric acid, 1 per cent., at 63°	17·5

	Millimeters.
Sulphuric acid, 0·1 per cent., at 63° . . .	17·4
Sulphuric acid, 1 per cent., at 63° . . .	16·35
Sulphuric acid, 5 per cent., at 63° . . .	16·65
Sulphuric acid, 10 per cent., at 63° . . .	16·25
Sulphuric acid, undiluted (HO SO_3), at 63° . . .	8·1
Oxalic acid, 1 per cent., at 66° . . .	17·35
Oxalic acid, 4 per cent., at 62° . . .	17·2
Ammonia, 0·1 per cent., at 66° . . .	16·65
Ammonia, 1 per cent., at 66° . . .	16·15
Ammonia, 12 per cent. (0·943 sp. gr.), at 66° . . .	15·05
Sugar, 10 per cent., at 65° . . .	16·3
Alcohol, 0·8 per cent. (0·9985 sp. gr.), at 60° . . .	15·5
Alcohol, 4·5 per cent. (0·992 sp. gr.), at 63° . . .	13·2
Alcohol, 7·8 per cent. (0·987 sp. gr.), at 60° . . .	11·05
Alcohol, 71 per cent. (0·869 sp. gr.), at 63° . . .	6·

Alcohol falls in the greatest degree below water in capillarity, yet the former substance is one of the least remarkable for the power to occasion osmose.

FIG. 1.



The newer facts to be related also increase the difficulties of the capillary theory of osmose.

My own experiments on osmose were made with both mineral and organic septa.

1. A convenient earthenware or baked clay osmometer is easily formed by fitting a glass tube and cover to the mouth of the porous cylinder, often used as a cell in Grove's battery, as in Fig. 1; the cylinder was generally five inches in depth by 1·7 inch in width, inside measure, and was capable of holding about six ounces of water. Gutta percha is much preferable to brass as the material for the cap or cover. The glass tube above was also comparatively wide, being 0·6 inch or 15 millimeters in diameter, and was divided into millimeters. It was not more than 6 inches in length. Each of the divisions or degrees amounted approximatively to $\frac{1}{750}$ th part of the capacity of the clay cylinder.

In conducting an experiment, the cylinder, always previously moistened with pure water, was filled with any saline solution to the base of the glass tube, and immediately placed in a jar of distilled

water, of which the level was kept adjusted to the height of the liquid in the tube of the osmometer throughout the whole experiment, so as to prevent inequality of hydrostatic pressure. The volume of water in the jar was comparatively large, fifty to eighty ounces. The rise or fall of the liquid in the tube was noted hourly for five hours. This rise commenced immediately, and was pretty uniform in amount for each hour during the short period of the experiment. The object aimed at was to observe the osmose of the solution before its composition was materially altered by dilution and the escape of salt by diffusion. The quantity of salt diffused from the osmometer into the water-jar during the experiment was also observed. After every experiment the osmometer was washed out by distilled water, which was allowed to permeate the porous walls of the cylinder, under the pressure of a column of water of about 30 inches in height, for eighteen hours. All the experiments were made at a temperature between 56° and 64° . The clay osmometer attained a considerable degree of uniformity in its action, when the same saline solution was diffused from it once in each of two or three successive days, with a washing between each experiment. A single observation is not much to be relied upon, as the first experiment often differs considerably from the others. One per cent. solutions were always used when the proportion of salt is not specified. Much larger proportions of salt have hitherto been generally employed, but it was early observed that the osmose absolutely greatest is obtained with small proportions of salts in solution. One part of salt to 400 water gives a higher osmose in earthenware than any other proportion for the great majority of substances. Osmose appeared, indeed, to be peculiarly the phenomenon of dilute solutions.

With the same proportion (1 per cent.) of different substances, the osmose varied from 0 to 80 degrees. Occasionally, instead of a rise of liquid in the tube, a fall was observed; the fall may be spoken of as negative osmose, to distinguish it from the rise or positive osmose.

Soluble substances of every description were tried, and find a place in the following classes:—

1. Substances of small osmotic power in porous earthenware; osmose under 20 of the millimeter degrees (ms.)

This class appears to include nearly all neutral organic substances, such as alcohol, pyroxylic spirit, sugar, glucose, mannite, salicin, amygdalin, salts of quinine and morphine, tannin, urea; also certain active chemical substances, which are not salts nor acids; chlorine water, bromine water.

The great proportion of neutral salts of the earths and metals proper also belong to the same class, such as chloride of sodium, of which the positive osmose was greatest in a solution containing no more than 0.125 per cent., being 19 ms. with that proportion of salt, but falling off and often becoming slightly negative with 1 per cent.

and higher proportions of salt in solution. Chloride of potassium is similar.

Nitrate of soda gave an osmose of 8, nitrate of silver of 18 ms.

The salts of the magnesian oxides are all low and sometimes slightly negative. Chlorides of barium and strontium both gave 18 ms.; nitrate of strontia, 5 ms.; sulphate of magnesia, 0.5 per cent., 2 ms.; 2 per cent., 3 ms.; sulphate of zinc was very similar, +2 to -2 ms., from 0.5 to 2 per cent.; chloride of mercury, 1 per cent., gave 6 and 8 ms. in two experiments.

2. Substances of an intermediate degree of osmotic force; osmose from 20 to 35 degrees. Sulphurous acid gave 20 ms. Certain vegetable acids have a similar osmose. Tartaric acid, in solutions of 0.25, 1, and 4 per cent., gave 24, 26, and 28 ms.; citric acid, 1 per cent., 30 ms. Also monobasic acids, such as hydrochloric acid, nitric acid, acetic acid, have the same moderate osmotic action in porous earthenware.

3. Substances of considerable osmotic power in porous earthenware; osmose from 35 to 55 ms.

In this class are found the polybasic mineral acids: sulphuric acid, 0.5 per cent., gave even 63 ms.; 2 per cent., 54 ms., or nearly the same osmose as the smaller proportion of acid.

In another earthenware cylinder, the following observations on the osmose of sulphuric acid were successively made:—

	Millimeters.
0.1 per cent.	43 and 43
1 per cent.	40 and 40
4 per cent.	41 and 39
10 per cent.	38 and 39

The results exhibit much similarity of osmose through a great range (1 to 100) in the proportion of acid. So small a quantity of this acid as one part in 1000 water, appears to give as great an osmose as any larger proportion of acid.

Certain neutral salts, sulphate of potash, sulphate of soda, sulphate of ammonia, belong to the same class.

With sulphate of soda the osmose for the different proportions 0.125, 0.25, 1, and 4 per cent. of salt, was 46, 47, 36, and 24 ms. respectively; the osmose diminishing with the increased proportion of salt.

Of sulphate of potash, 0.25 per cent. gave 51 ms.; 1 per cent. 46 ms., and 4 per cent. 38 ms., showing no great change from one quarter to 4 per cent.; chromate of potash, 1 per cent., gave an osmose of 54 ms.

4. Substances exhibiting the highest degree of osmotic power in porous earthenware.

Salts of the alkalis, possessing either a decided acid or alkaline reaction, and certain neutral salts of potash.

Binarsenate of potash gave 66 ms.; Rochelle salt 82 ms.

With binoxalate of potash the osmose observed in an earthenware osmometer was—

	Millimeters.
For 0.02 per cent.	32
0.05 per cent.	55
0.1 per cent.	63
0.25 per cent.	70 (highest)
1 per cent.	63
2 per cent.	56

Of salts having alkaline properties, phosphate of soda gave 70.5; borax, carbonate of soda, and bicarbonate of soda, all gave numbers which ranged above 60 ms. in various osmometers.

To the same class also belong certain strong acids, phosphoric acid giving an osmose of 62 ms., glacial phosphoric acid of 73 ms.

The caustic alkalis have probably too strong a disorganizing action upon the septum to allow osmose to proceed undisturbed. They give a positive osmose when present in a minute proportion, but very soon attain their *terme moyen*, and then become slightly negative.

Caustic soda, 0.01 per cent., gave 24 ms.; 0.02 per cent., 29 ms.; 0.05 per cent., 31 ms., which was the highest osmose observed; 0.1 per cent., 22 ms.; 0.25 per cent., 3 ms.; 1 per cent. and 2 per cent. of caustic soda gave both —10 ms.

It appears most clearly that highly osmotic substances are also chemically active substances. Both acids and alkaline substances possess the affinities which would enable them to act upon the silicates of lime and alumina, which form the basis of the earthenware septum. Lime and alumina were accordingly found in solution after osmose, and the corrosion of the septum appeared to be a necessary condition of the flow.

It was found impossible to exhaust the whole soluble matter of the walls of the earthenware osmometer, by washing, either with water or with a dilute acid, for the process of decomposition appeared to be interminable. After such washings the action of an osmometer was often greatly modified upon salts of moderate osmose, such as chloride or sodium; and similar changes gradually took place in the osmometers when used in ordinary experiments with saline solutions.

It is on this account that I avoid the lengthened detail of numerous experiments which were made with the earthenware osmometer, and confine myself to general statements.

Further, the potash salts were also largely kept back or absorbed by the earthenware, a phenomenon of the same class as the retention

of alkalies by aluminous soils, which has been studied by Messrs. Thomson and Way.

Other septa, which were not acted upon by the salts, were found deficient in osmotic activity, although possessed of the requisite degree of porosity. Gypsum, compressed charcoal, and tanned sole-leather, gave rise to no osmose when permeated by saline solutions. White plastic clay had an osmotic power which was quite insignificant when compared with that of baked clay: now the former may be considered as an aluminous compound, upon which the decomposing action of water has been already exhausted, while the latter is in a form more liable to decomposition, in consequence of an effect of heat upon the constitution of the aluminous silicates of the clay. A plate of Caen stone, which is an impure limestone, was greatly more active with a solution of carbonate of potash than a plate of pure white marble was. The effect of impurities in making limestone suitable for osmose did not escape the observation of Dutrochet; it was referred by him to the attraction of alumina for water. Mere capillarity, therefore, is insufficient to produce the liquid movement, while the *vis motrix* appears to be some form of chemical action.

For the proper appreciation of a chemical theory of the osmotic force, I would now invite attention to a purely speculative subject, namely, the molecular constitution of water and saline solutions. Allowing that water, in the state of vapour, is correctly represented as a compound of one equivalent of oxygen and one of hydrogen, it may still be true that the molecule of *liquid water* is a varying aggregate of many such molecules, or is n times HO. But if so much is conceded, a new and peculiar grouping of the atoms of oxygen and hydrogen becomes not only possible, but probable. Instead of arranging them in a series of pairs of $H + O$, $H + O$ in our compound molecule, we may give a binary form to that molecule in which a single atom of oxygen is the negative or chlorous member, and the whole other atoms united together form a positive or basylous radical. In this radical we have a certain multiple of HO with one H in excess, the last condition being most usual in compound radicals, such as ethyl, methyl, benzoyl, &c., which have all a single unbalanced equivalent of hydrogen; $H_nO_n = (H_{m+1}O_m) + O$.

Further, this new oxide should be more easily decomposed than oxide of hydrogen, HO. The basicity of the radical $(H_{m+1}O_m)$ depends upon the disproportion of the equivalents of oxygen and hydrogen in its constitution, there being one of hydrogen in excess. Now that disproportion becomes less as we ascend, as in $3H + 2O$, $11H + 10O$, $101H + 100O$; and the more feeble the basyl-atom, it may be supposed to retain less forcibly its fellow oxygen-atom or other negative element with which it is combined. When water, therefore, has to undergo decomposition in a voltaic circle, it will naturally assume the molecular

arrangement supposed, as being the binary form which is most easily divisible into a positive and negative element, or that in which water is most easily decomposed.

This molecular view has been brought forward at present principally for the aid which it gives in conceiving what is known as electrical endosmose.

This interesting phenomenon, first well developed by our colleague Mr. Porrett, has very lately been defined with great clearness by M. Wiedemann.* The water which accumulates at the negative pole (or follows the hydrogen), in the electrolysis of the pure liquid, is found to be exactly proportional to the amount of circulating affinity; that is, with every equivalent of hydrogen that is discharged at the negative pole the same quantity of water arrives there, and will force its way through a porous diaphragm to reach that destination. The reason now suggested is, that the travelling basylous atom in the voltaic decomposition is not hydrogen simply, but the voluminous basylous molecule ($H_{m+1}O_m$) above described; which again breaks up at the negative pole into hydrogen and water, ($H_{m+1}O_m$) = mHO and H .

But even although such a representation of the circumstances of electrical endosmose may not be fully admitted, the phenomenon itself is of great service to us, as showing that in the occurrence of chemical decompositions affecting ultimate particles, sensible volumes of water may be involved and set in motion.

Further, in considering the action of chemical affinity between bodies in solution, between an acid and alkali for instance, we are apt to confine our attention to the principal actors in the combination, and to neglect entirely their associated water of hydration. Yet both the acid and base may have large trains of water attached to them by the tie of chemical union. Sulphuric acid certainly evolves heat with the fiftieth equivalent of water that is added to it, and probably in dilute solution that acid is capable of having a still greater number, indeed an indefinitely large number, of equivalents of water combined with it. In fine, there is reason to believe that chemical affinity passes, in its lowest degrees, into the attraction of aggregation.

The occurrence of chemical decomposition within the substance of a porous resisting septum may be calculated to bring into view the movement and disposal of the water chemically associated in large quantities with the combining substances; as the interposition of a porous diaphragm in electrical endosmose makes sensible a translation of water in voltaic decompositions which is not otherwise observable.

II. The osmose of liquids has hitherto been principally studied in septa of *animal membrane*, which from their thinness, their ready permeability combined with a sufficient power of resistance to the

* Pogg. Ann. lxxxvii. 321.

passage of liquids under pressure, have great advantages over mineral substances.

The great proportion of the experiments of the present inquiry were also made with animal membrane.

The membrane osmometer employed, which is only a modification of the classical instrument of Dutrochet, was prepared as follows:—

The mouth of a little glass bell-jar A (fig. 2) had first loosely applied to it a plate of perforated zinc B slightly convex, and then the membrane was tied tightly over the latter for the sake of support (fig. 3). The

FIG. 2.



FIG. 3.



quantity of metal removed in the perforations of the zinc plate amounted to 49 per cent. of the weight of the zinc. This plate was always varnished or painted, to impede, if not entirely prevent, the solution of the metal by acid fluids. The usual diameter of the bulb was about 3 inches or 75 millimeters, and its capacity equal to 5 or 6 oz. of water. The tube C was usually not more than 6 inches in length, but comparatively wide, its diameter being about 7.5 millimeters, that is, one-tenth of the diameter of the mouth of the bulb, and it was divided into millimeters. The action of an osmometer depends chiefly upon the extent of membrane-surface exposed, and very little upon the capacity of the instrument. Hence the relation of diameters (or areas) between the bulb and tube was adopted in preference to the relation in capacity, the area of the section of a tube being one-hundredth of the area of the disc of membrane, or rather it was reduced by calculation to this relation by means of a coefficient for each instrument.

Hence a rise of liquid in the tube amounting to 100 millimeters indicates the admission into the bulb of a sheet of water of 1 millimeter (one twenty-fifth part of an inch) in depth, over the whole surface of the membrane, and so in proportion for any other rise in the tube. These millimeter divisions (ms.) of the tube mark, therefore, degrees of osmose which have an absolute and equal value in all instruments. The bulb of the instrument filled with the solution to be operated upon was placed within a cylindrical glass jar of distilled water, containing at least sixty ounces (fig. 4), and during the experiment

FIG. 4.



inequality of hydrostatic pressure was carefully avoided by maintaining the surface of the water in the jar at the level of the liquid in the tube. The osmometer was supported upon a tripod of perforated and painted zinc, at a height of about 4 inches from the bottom of the glass cylinder. The osmose was observed hourly for five hours, during which time it advanced in general with considerable uniformity. In an experiment with fresh ox-bladder as the septum, and a solution of 1 per cent. of carbonate of potash in the osmometer, the rise in five consecutive hours was 10, 12, 11, 14, 13 millimeter degrees, and in five hours immediately following, 13, 12, 9, 11, and 12 millimeter degrees, making sixty degrees in the first, and fifty-seven degrees in the second period of five hours. The quantity of salt which diffused outwards during the experiment of five hours was also frequently determined, usually by evaporating the liquid of the water-jar to dry-

ness; it rarely exceeded one-tenth part of the salt originally present in the osmometer. The membrane itself was also weighed before it was applied to the osmometer, and again when its use was discontinued, which was generally after six or eight experiments had been made with the membrane. A loss of the substance of the membrane was always observed, varying from 20 to upwards of 40 per cent. of its original weight.

The outer muscular coat of bladder soon becomes putrescent, and from changes in its consistence, and the large quantity of salts and

other soluble substances which it yields by decomposition, gives occasion to much irregularity in the experiments. The great change in the amount of osmose often produced by merely turning the membrane, observed by M. Matteucci and others, depends often, I believe, upon the soluble matter of the muscular coat being thrown outwards or inwards, according as the membrane is applied. The muscular coat was on this account removed from the ox-bladder employed, and the serous membrane remaining found to acquire greatly increased activity, and also to act with much greater regularity in successive experiments. The membrane so prepared could be used for weeks together without the slightest putrescence of any part of it. Two of these thin membranes, or a double membrane, were often applied. The weight of a disc of single membrane, $4\frac{1}{2}$ inches in diameter in a dry state, varied from about 0.5 to 1.2 gramme. The soundness of the membrane of an osmometer and its degree of permeability were always roughly tested before an experiment, by filling the bulb, without its tube, completely with water, hanging it up in air, and observing how frequently a drop fell from the instrument. The time between each drop varied, with suitable membranes, from one to twenty minutes. The times in which water permeated the same membranes by osmose varied between much narrower limits, perhaps from one to two.

The quantity of salt which traversed different membranes by diffusion, was also found to be in proportion to the osmotic permeability of the membranes, and not to their mechanical porosity.

To wash the membranes, they were macerated in distilled water after every experiment for not less than eighteen hours, without being ever removed from the glass bulb. A membrane also was never allowed to dry, but was kept humid as long as it was in use for experiments.

Osmose in membrane presented many points of similarity to osmose in earthenware. The membrane was constantly undergoing decomposition, soluble organic matter being found both in the fluid of the osmometer and in the water of the outer jar after every experiment; and the action of the membrane appeared to be exhaustible, although in a very slow and gradual manner. Those salts and other substances, of which a small proportion is sufficient to determine a large osmose, are, further, all of the class of chemically active substances, while the great mass of neutral organic substances and perfectly neutral monobasic salts of the metals, such as the alkaline chlorides, possess only a low degree of action.

When a solution of the proper kind is used in the osmometer, the passage of fluid proceeds with a velocity wholly unprecedented in such experiments. Take, for instance, the rise in five hours exhibited in a series of experiments upon solutions of several different proportions of carbonate of potash, made in succession with the same membrane in the order in which they are related.

	Millimeters.
With 0·1 per cent. carbonate of potash, a rise of	182
With 0·1 per cent. carbonate of potash, a rise of	120
With 0·1 per cent. carbonate of potash, a rise of	199
With 0·5 per cent. carbonate of potash, a rise of	246
With 0·5 per cent. carbonate of potash, a rise of	194
With 1 per cent. carbonate of potash, a rise of	205
With 1 per cent. carbonate of potash, a rise of	207

Or the rise in the same time with another membrane which had been previously exposed to a steam heat of 212° for ten minutes without impairing its activity.

	Millimeters.
With 1 per cent. carbonate of potash at 60° F., a rise of	402
With 0·1 per cent. carbonate of potash at 60° F., a rise of	196
With 0·1 per cent. carbonate of potash at 60° F., a rise of	153
With 2 per cent. carbonate of potash at 60° F., a rise of	511
With 4 per cent. carbonate of potash at 60° F., a rise of	781
With 10 per cent. carbonate of potash at 60° F., a rise of	863

In the last experiment a rise of fluid in the tube of upwards of 30 inches occurs in five hours, and so much water is impelled through the membrane as would cover its whole surface to a depth of 8·6 millimeters, or one-third of an inch. Both membranes, but particularly the first, show the comparatively great activity of small proportions of salt, the average osmose of 0·1 per cent. of carbonate of potash in the first osmometer being 167 millimeter degrees, and of 1 per cent. 206 millimeter degrees.

Now the quantity of carbonate of potash which diffuses out of the osmometer into the water-jar was determined by the alkalimetric method in the second and third of the 0·1 per cent. observations first related, and found to be in both cases 0·018 gramme (0·28 grain); the quantity of water also which entered in return can be calculated from the known capacity of the tube of the osmometer, of which each millimeter division represented 0·060 gramme of water; and consequently 167 divisions represent 10·020 grammes (155 grains) of water. We have, in 0·1 per cent. solution,—

Mean diffusate of carbonate of potash .	0·018 grm. =	1
Mean osmose (of water)	10·020 grms. =	556

The conclusion is, that while the membrane was traversed during the five hours of an experiment by 1 part of carbonate of potash passing outwards, it was traversed by 556 parts of water passing inwards.

In the two experiments with 1 per cent. solution of carbonate of potash in the same osmometer, the diffusates were 0·192 and 0·198 gramme of carbonate of potash, which are sensibly ten times greater than the diffusates of the 0·1 per cent. solution. But the mean osmose

of the 1 per cent. solutions is greater than that of the 0.1 per cent. solutions only in the proportion of 206 to 167, or as 1 to 0.81. The ratio in question, however, varies greatly in different membranes. We have, consequently, in 1 per cent. solution,—

Mean diffusate of carbonate of potash	. 0.195 grm. = 1
Mean osmose (of water)	. 12.360 grms. = 63.4

Whatever, therefore, be the nature of the chemical action occurring in the membrane which influences osmose, a minute amount of that action appears to be capable of producing a great mechanical effect.

All idea of contractility or organic structure being the foundation of the osmotic action of membrane, was excluded by the observation that similar large effects could be obtained from a septum of pure coagulated albumen.

A convenient albumen osmometer is constructed by covering the opening of the bulb of the former instrument by ordinary thin cotton calico, which is best applied wet, and painting over the outer surface of the calico two or three times with undiluted egg albumen, an hour being allowed to elapse between each application of the albumen. The instrument is then suspended in the steam rising from boiling water for a few minutes, so as to completely coagulate the albumen. The albuminated calico may then be macerated for twenty-four hours before use, by placing the osmometer in cold water, to dissolve out the soluble salts of the albumen. It should be preserved always in a humid state. Before application to the calico, the albumen in many cases was neutralised with acetic acid, and filtered, the more completely to obliterate every trace of organic structure.

The osmose in a particular instrument of this kind was, at 50°, for

	Millimeters.
1 per cent. carbonate of potash	. 211
1 per cent. carbonate of potash	. 367
1 per cent. carbonate of potash	. 387
0.1 per cent. carbonate of potash	. 127
0.1 per cent. carbonate of potash	. 124

The correct rate is rarely obtained in the first observation, as seen above, in osmometers of albumen as well as of other materials.

The albumen plate has generally a greater thickness than prepared membrane, which appears to diminish proportionally the quantity of salt which escapes by diffusion.

The diffusate in the three experiments above of 1 per cent. carbonate of potash was 0.024, 0.038, and 0.042 grm. of the salt. The largest proportion of carbonate of potash (0.042 grm.) which was

obtained in the last of the three experiments was replaced by 23.220 grms. of water, or 552 times the weight of the salt.

An obvious and essential condition of osmose is difference of composition in the two fluids in contact with the opposite sides of the porous septum. With the same solution, or with pure water, in contact with both surfaces of a membrane there may be no chemical action, but it will be equal on both sides, and although probably attended with movements of the fluids, yet nothing will be indicated, as the movements, being equal and in opposite directions, must neutralise each other. Difference of composition in the two fluids is necessary in order that there may be inequality of action upon the two sides of the membrane. It is difficult, however, with respect to the chemical action, to ascertain either its true sphere or its exact nature. No substance appears to be permanently deposited in the membrane during osmose, even by easily decomposed metallic salts, such as salts of lead and mercury. The action upon the membrane is probably of a solvent nature, and its seat may possibly be ascertainable when two membranes are used together. Some observations made on the comparative loss of weight of the outer and inner membrane have not, however, shown any remarkable difference. But this again may arise from the great proportion of the loss in both membranes being due to the ordinary solvent action of water alone, and the operative solvent action of the osmotic salt being comparatively minute in amount; or it may depend, and I am most inclined at present to take this view, upon the chemical actions being of a different kind on the two sides of the membrane, and not upon the inequality simply of one kind of action. Such a supposition was suggested by the fact, which will immediately appear, that osmotic activity and easy decomposition are properties often found together in binary compounds. The basic and acid agents then developed are both capable of acting upon albuminous septa. We may imagine, for instance, in the osmotic action of a neutral salt, the formation within the thickness of the septum of a polar circle, one segment of which (composed of the binary molecules of the salt) presents a basic molecule to the albumen at the inner surface of the septum, and an acid molecule to the albumen at the outer surface, the circle being completed through the substance of the septum which forms the second segment. Both surfaces of the septum would be acted upon, but at one side we should have combination of the albumen with an alkali, on the other side with an acid. This, however, must be taken as a purely ideal representation of the condition of the septum in osmose. I have not discovered such a polar condition of the septum, and I doubt whether the galvanometer could be properly applied to exhibit it, as the placing of the poles of that instrument in the dissimilar fluids existing on opposite sides of the septum would alone be sufficient to give

rise to voltaic polarisation. At present I must confine myself to the enunciation of certain general empirical conclusions respecting the operation of chemical affinity in osmotic experiments.

With animal septa, frequent examples of the outward flow of liquid from the osmometer present themselves, causing the liquid column to fall instead of rise in the tube. This phenomenon (exosmose) I have spoken of as negative osmose. The observation of Dutrochet, that oxalic acid in the osmometer, and also tartaric acid at a certain point of concentration, give rise to negative osmose, I have been able to generalise in so far as acids have universally either a negative osmose, or lie at the very bottom of the positive class.

Oxalic acid gave in membrane, for 1 per cent. acid, -148 ms. and -141 ms.; and for 0.1 per cent., -10 and -27 ms. In another membrane, 1 per cent. of the same acid alone gave -136 ms.; with the addition of 0.1 per cent. hydrochloric acid, -181 and -168 ms. By the addition of 0.1 per cent. of chloride of sodium, a salt which in small proportions is nearly neutral to osmose, the negative osmose of 1 per cent. oxalic acid fell in the same membrane to -45 ms., and with the addition of 0.25 per cent. of chloride of sodium the osmose was $+6$ ms., or became slightly positive. The negative osmose of 1 per cent. of oxalic acid, in a membrane where it amounted to -56 and -57 ms. in two experiments, became, with the addition of 0.1 per cent. of albumen -46 ms.; of 0.25 per cent. of albumen -20 ms.; of 0.25 per cent. of gelatin -59 ms., and of 0.25 per cent. of sugar -53 ms.

In albuminated calico, the osmose of 1 per cent. of oxalic acid was also negative, namely -13 , -16 and -20 ms. in three successive observations. With the addition to the oxalic acid of 0.1 per cent. hydrochloric acid, the osmose became -46 and -58 ms.; and with the addition of 0.1 per cent. of sulphurous acid, the osmose became -62 and -58 ms.

Of *hydrochloric acid* introduced into the membrane-osmometer in the small proportion of 0.1 per cent., the negative osmose was -92 , -37 and -27 ms. in three successive experiments. The negative osmose of hydrochloric acid was still more powerfully counteracted than that of oxalic acid, by the association of a minute proportion of chloride of sodium with the acid. The negative osmose of this acid appears to be extremely precarious. It is reversed by a great variety of neutral soluble substances, and on that account can rarely be observed at all with bladder undivested of its muscular coat.

In a certain prepared membrane, *sulphuric acid*, 0.1 per cent., gave an osmose of -4 , $+8$ and $+7$ ms.

Nitric acid, 0.1 per cent., gave an osmose, at 58° , of $+8$ and $+23$ ms.

Tribasic phosphoric acid, 1 per cent., gave -6 and -7 ms., at 61° and 63° . The diffusates of phosphoric acid, in the same experiments, amounted to 0.143 and 0.130 grm.

The *glacial or monobasic phosphoric acid*, 1 per cent., gave $+137$ and $+131$ ms., at 55° , which is a considerable positive osmose, an interesting circumstance when taken in connexion with the deficient acid character of that modification of phosphoric acid. The same acid, 0.1 per cent., gave a positive osmose in the last membrane of 28 and 23 ms.

Citric acid, 1 per cent., gave 39 and 36 ms.; 31 and 31 ms., at 62° ; the first in membrane and the second in albumen.

The same acid, 1 per cent., after being fused by heat, gave, at 63° , -38 and -35 ms. in membrane; 0 m. and -2 ms. in albumen.

A small proportion of fused citric acid, 0.1 per cent., gave on the other hand a slight positive osmose, namely 15 ms. and 2 ms. in the previous membrane and albumen osmometers respectively.

Tartaric acid, 1 per cent., gave 18 and 19 ms. in membrane, at 68° ; with 20 ms. in albumen, at 62° .

The same acid, after being fused by heat, gave -68 and -61 ms. in membrane, at 57° , showing a molecular change from fusion, as in citric acid.

The diffusate in the last two experiments was 0.123 grm. and 0.132 grm. of acid.

In albumen the osmose of fused tartaric acid remained slightly positive, being 5 and 2 ms. for 1 per cent., at 60° , and 5 and 3 ms. for 0.1 per cent., at the same temperature.

Racemic acid, 1 per cent., gave 4 , 11 , and 7 ms. in three experiments, at 55° , in the last-used membrane; with 15 and 22 ms. at the same temperature in albumen; or was always slightly positive, like tartaric acid.

Acetic acid, in the proportions of 0.1 , 0.5 , and 1 per cent., gave sensibly the same small positive osmose, 25 to 28 ms., at 57° to 62° , in membrane.

A saturated solution of *carbonic acid* in water gave 25 and 26 ms. in membrane, with 20 and 22 ms. in albumen, both at 65° .

The last solution, diluted with an equal bulk of water, gave an osmose of 15 and 11 ms. in membrane, and 16 ms. twice in albumen, both at 63° .

Terchloride of gold is negative in its osmose, like the stronger acids, giving -49 and -54 ms. in membrane, at 64° , with much reduction of metallic gold in the substance of the membrane.

Bichloride of platinum, made as neutral as possible by evaporation, gave for the 1 per cent. solution -32 and -30 ms. in membrane, at 61° . For the 0.1 per cent. solution, a positive osmose of 27 , 14 , and 5 ms. in three successive experiments made with the last membrane,

at 64°, 65°, and 62°. The same 1 per cent. solution gave in albumen, at 61°, a positive osmose of 54 and 50 ms.; the 0.1 per cent. solution also, at 64°, gave 43 ms. Albumen appears thus to be less adapted for bringing out the negative osmose of various substances than membrane is.

In membrane, *bichloride of tin*, 0.1 per cent., gave 24 ms., at 61°; 1 per cent. —46 and —71 ms., at 59°. The addition to the last of 0.5 per cent. of sulphuric acid gave —63 ms., or did not alter the character of the osmose. But partial neutralisation of the 1 per cent. tin solution by ammonia, on the other hand, gave 0 m., or destroyed all osmose. One per cent. of bichloride of tin gave only a small negative osmose in albumen, namely 5 ms. twice, at 59°.

Oxalic acid carries the highly negative character of its osmose into the *binoxalate of potash*, of which 1 per cent. of anhydrous salt gave in membrane —112 and —99 ms., at 62°; 0.1 per cent., —30 ms., at 60°. One per cent. of the same salt in albuminated calico gave —20 ms., at 60°. A saturated solution of binoxalate of potash, containing 2.5 per cent. of salt, gave —15 ms. in the last osmometer.

Bisulphate of potash, 1 per cent., gave 4 and 7 ms. in membrane, at 56°; in albumen, 7, 3 and 6 ms., at 56°.

A solution of *bitartrate of potash*, saturated in the cold, also gave a small positive osmose, namely 4 and 2 ms. in membrane, and 20 and 17 ms. in albumen, both at 56°. Other supersalts tried gave also a small positive osmose, such as binarsenate of potash and bichromate of potash. It becomes doubtful, therefore, whether any of the supersalts of potash are negative, except the acid oxalates of that base.

Neutral organic substances dissolved in water appear to be generally deficient in the power to give rise in membrane to that osmose which depends upon a small quantity of the soluble substance, such as 1 per cent., or a still less proportion. The osmose obtained in ox-bladder employed without removing the muscular coat, was, in 1 per cent. solutions of the substances, salicin 5 ms., tannin 3 ms., urea 4 ms., gelatin 9 ms., amygdalin 6 ms., lactine 7 ms., gum-arabic 18 ms., and hydrochlorate of morphine 4 ms.

The relations to osmose of alcohol and sugar were more fully examined. With these and other chemically inactive substances, the osmose, although small for 1 per cent., increases progressively with larger proportions of the substance, and also bears a close relation to the proportion of substance diffused outwards, circumstances which give a mechanical character to the osmose. It is with such substances that the influence of diffusibility upon osmose is most likely to betray itself. They have a peculiar interest in the study of the phenomenon, as they present a certain small but remarkably uniform

amount of osmose without the known intervention of any strong chemical affinities.

Alcohol.—In describing an experiment I shall endeavour to put forward all the circumstances which can be supposed to influence in any way the result.

In the table which follows, Column I. contains the proportion of absolute alcohol, by weight, which is dissolved in the water of the osmometer.

A 10 per cent. solution is prepared by weighing 10 grammes of the substance, and then adding water to it so as to make up the liquid to the volume of 100 grammes of water. It is necessary to make up in this way solutions used in experiments of diffusion and osmose, in order to preserve a true relation in solutions containing the different proportions of substance, for it is a fixed volume (not weight) of these solutions which must be used in the osmometer. We come thus to have with a 20 per cent. solution of alcohol exactly twice as much alcohol in the osmometer as with a 10 per cent. solution of alcohol, and so of other proportions.

The membrane of the osmometer is always to be considered as fresh, or as used for the first time in the first experiment narrated, and the observations to be made successively as they stand in the table. The length of maceration in cold water to which the membrane has been exposed previous to the osmotic experiment, as before described, is given in Column V. By the most frequent time of one day is to be understood the space of eighteen hours which intervened between experiments on successive days.

The hydrostatic resistance of the membrane given in Column VI. is the length of time, in minutes, observed to elapse between the fall of two drops from the bulb of the osmometer filled with distilled water, and hung up in air as already described. The temperature of the water in the glass cylinder during the experiment is noted in Column VII.; the rise of fluid in the tube of the osmometer or osmose, in millimeter divisions of the tube, appears in Column II., and the absolute amount of the same osmose is expressed in Column III. in grammes, or more strictly in gramme measures of water. Lastly, the weight of diffusate found in the water of the glass cylinder appears in Column IV. These last two data, the osmose and diffusate, both in grammes, afford the means of comparing the weight of substance which has escaped from the osmometer, with the weight of water which has entered the osmometer in the same time. It is necessary, however, to recollect, that the apparent osmose or rise observed is only the excess in volume of the liquid which has entered, over the volume of the liquid which has left the osmometer. To obtain the full volume of water which has entered (the true osmose), it is therefore necessary to add the bulk of the substance diffused to the osmose observed.

TABLE I.—Alcohol in Osmometer A of double membrane during five hours.

I.	II.	III.	IV.	V.	VI.	VII.
Alcohol in solution.	Rise or osmose in millimeter degrees.	Rise or osmose in grammes of water.	Diffusate of alcohol in grammes.	Previous maceration of membrane.	Hydrostatic resistance of membrane.	Temperature, Fahr.
per cent.				days.	min.	°
0.25	12	—	—	1 $\frac{1}{2}$	8	63
0.25	7	—	—	1	8	63
1	10	—	—	1	6	66
1	15	—	—	1	6	66
2	20	—	—	1	6	67
2	22	—	—	1	6	69
5	45	1.984	0.521	2	6	72
5	45	1.984	0.452	1	8	70
10	70	3.072	—	1	8	67
10	76	3.328	—	1	8	67
20	107	4.672	—	1	8	67
20	109	4.800	—	1	8	67

A second series of observations was made simultaneously, in another membrane osmometer, in order to ascertain the degree of concordance to be expected in such experiments.

TABLE II.—Alcohol in Osmometer B of double membrane for five hours.

I.	II.	III.	IV.	V.	VI.	VII.
Alcohol in solution.	Rise or osmose in millimeter degrees.	Rise or osmose in grammes of water.	Diffusate of alcohol in grammes.	Previous maceration of membrane.	Hydrostatic resistance of membrane.	Temperature, Fahr.
per cent.				days.	min.	°
1	14	—	—	2 $\frac{1}{2}$	12	63
1	14	—	—	1	12	63
2	19	—	—	1	8	66
2	19	—	—	1	8	66
5	46	—	—	1	8	67
5	54	2.432	0.579	1	8	69
10	90	4.028	1.505	2	6	72
10	96	4.332	—	1	8	70
20	120	5.396	—	1	8	67
20	123	5.472	—	1	4	67
20	137	6.156	—	1	4	67
20	142	6.384	—	1	4	67

It will be observed that the osmose increases with the proportion of alcohol, but not in so rapid a ratio; the osmose of the 20 per cent.

solution being about only ten times greater than that of the 1 per cent. solution in both series. The hydrostatic resistance of the membrane B falls off in a remarkable manner in the later experiments, indicating an increased facility of permeation, which may influence the increased osmose in the last two observations of this series. The results otherwise of the two series exhibit a fair amount of correspondence, both in the degree of osmose and the amount of diffusate for the same proportions of alcohol in the two osmometers. It should be added, that in several instances the water in the jars was changed after the third hour of the experiment, with the higher proportions of 10 and 20 per cent. The alcohol was determined, after it had been concentrated by two distillations, by means of Drinkwater's table of densities.

Several experiments were made to determine the proportion of the diffusate of alcohol from 5 and 20 per cent. solutions respectively of that substance, in membrane osmometers. The mean proportion was as 1 to 3.02, which is mentioned here, as I was led at first to a different conclusion by earlier and imperfect experiments.

Sugar.—The osmose of sugar in membrane was examined very fully, in the hope that the simple effect of diffusion would be exhibited without being modified by any chemical action, in a substance so entirely neutral.

Crystallised cane-sugar was made use of.

TABLE III.—Sugar in Osmometer D of double membrane for five hours.

I.	II.	III.	IV.	V.	VI.	VII.
Sugar in solution.	Rise in millimeter degrees.	Same in grammes of water.	Diffusate of sugar in grammes.	Previous maceration.	Hydrostatic resistance.	Temperature, Fahr.
per cent.				days.	min.	°
1	21	1.027	—	1	4	64
1	8	0.395	0.150	9	2½	63
1	19	0.948	0.140	1	3½	63
2	19	0.948	0.178	1	2½	66
2	19	0.948	0.182	1	2½	66
5	39	1.900	0.438	1	2½	67
5	49	2.370	0.480	1	2½	69
10	66	3.239	1.110	2	2½	72
10	79	3.871	0.853	1	2½	70
10	76	3.713	0.840	1	3	67
20	121	5.975	1.376	1	3	67
20	117	5.688	1.485	1	3	67

It was very desirable to find whether the deviations from a regular progression seen in the numbers for the osmose and diffusate in

the preceding results are essential, or accidental and peculiar to the present membrane. It was also desirable to find whether a membrane would stand the repetition of such a series of experiments and continue to give similar results. A double series of experiments were accordingly made with new membrane.

TABLE IV.—Sugar in Osmometer E of double membrane for five hours.

I.	II.	III.	IV.	V.	VI.	VII.
Sugar in solution.	Rise in millimeter degrees.	Same in grammes of water.	Diffusate of sugar in grammes.	Previous maceration.	Hydrostatic resistance.	Temperature, Fahr.
per cent.				days.	min.	°
0.25	5	0.240	—	2	10	63
0.25	9	0.420	0.050	1	10	63
1	12	0.531	0.110	1	8	66
1	11	0.472	0.106	1	10	66
2	24	1.060	0.205	1	8	67
2	31	1.357	0.208	1	8	69
5	65	2.891	0.600	2	8	72
5	63	2.773	0.555	1	8	70
10	89	3.953	1.073	1	10	67
10	104	4.602	0.967	1	10	67
10	96	4.248	—	1	10	67
20	133	5.900	1.457	1	10	67
20	106	4.720	1.643	10	10	64
20	118	5.251	1.656	1	6	64
1	19	0.826	1.105	1	6	68
1	19	0.826	—	1	6	65
2	24	1.062	0.153	1	6	65
2	25	1.121	0.162	1	6	64
5	37	1.652	0.435	2	8	66
5	33	1.425	0.470	1	8	67
10	69	3.068	0.757	2	8	67
10	76	3.363	—	1	8	69
20	110	4.807	—	1	8	70
20	112	4.956	1.540	2	3	70

The diffusates of sugar (Column IV.) were obtained by evaporating the fluid of the water-jar to dryness, at 212° , and therefore contain organic matter dissolved out of the membrane; the weight of each of the diffusates is increased by this addition a few thousandths, but not in such a quantity as to affect the result to an extent that is at all material, except in the first diffusate recorded, that from the 0.25 per cent. solution.

Although the results exhibit several irregularities, yet starting from the 1 per cent. observation, in the first series of Table IV., the amount both of osmose and diffusate appears compatible with an arithmetical progression in the observations from 1 to 10 per cent. Thus the average rise in the 1 per cent. solution is 11.5 millimeter

degrees, and in the 10 per cent. solution 96.3 ms.; the average diffusate in the 1 per cent. solution is 0.108 gramme, and in the 10 per cent. solution 1.020 gramme.

But with the 20 per cent. solution both osmose and diffusate fall off greatly, and the osmose more than the diffusate. The osmose of the 20 per cent. solution may be taken as 125 ms.,—the mean of the first and third observations, 133 and 118, the intermediate observation 106 being obviously exceptional, possibly from the unusually long maceration of the membrane immediately preceding that experiment. Hence the osmose only rises from 96.3 ms. to 125 ms., while the proportion of sugar in the osmometer was increased from 10 to 20 per cent.

The mean diffusate of sugar also increases with the same change only from 1.020 gramme to 1.585 gramme.

In the second series of observations with the same membrane, given in the lower part of the same Table, both the osmose and diffusate fall off, to an extent which is perhaps pretty fairly represented by the 10 per cent. solution, which gives a mean osmose of 72.5 ms. against 96.3 ms. in the former series, and a diffusate of 0.757 gramme against 1.020 gramme in the former series. A rough proportionality between the two series of observations is sufficiently indicated.

Two observations are recorded in the last series which must not be allowed to mislead. These are, the comparatively high osmose of 19 ms. for the 1 per cent. solution, which is accidental, and arises from the 1 per cent. experiments having been immediately preceded by the high proportion of 20 per cent. The other observation referred to is the high diffusate of the last 20 per cent. solution at the bottom of the table, which has no doubt been occasioned by the sudden diminution in the hydrostatic resistance of the membrane from 8 to 3 in that which is the last experiment of the series. The membrane, indeed, appears to be giving way after its long use, for the osmometer had been exposed to the action of water for thirty-five days without intermission.

The reason why the diffusion and osmose are smaller in the second series of experiments than in the first series (nearly as 3 to 4), is (I believe), that the membrane softens and swells somewhat by the protracted action of water; a change in the structure of the membrane which impedes diffusion by increasing the length of the channels through which the salt has to travel.

It may now be interesting to discover the proportion between the water which enters and the sugar which leaves the osmometer in these experiments. That proportion appears not to vary greatly in the range from the 1 to the 10 per cent. solution. For a mean result, the sum of the eight diffusates between 1 and 10 per cent. inclusive, in the first series of observations of Table IV., may be taken,

and the osmose belonging to the same experiments. There are so obtained 3·824 grammes of sugar diffused against an osmose of 17·639 grammes of water. But this, the apparent osmose, has to be increased by the bulk of the sugar diffused, which may be estimated at ten-seventeenths of its weight of water, or 2·25 grammes. Adding the last quantity to 17·639 grammes, we obtain—

Sugar or diffusate	3·824 grm. = 1
Replacing water	19·889 grm. = 5·2

Hence the sugar appears to be replaced in osmose by rather more than five times its weight of water. The less complete experiments with alcohol, previously described, indicate a nearly similar relation to its replacing water.

Calculating, in like manner, the observations made upon each of the five proportions of sugar in Table III., we obtain numbers for the replacing water which oscillate about the general result first stated : the mean diffusates of sugar and amounts of replacing water were in the different solutions :—

In 1 per cent. solution, 0·145 grm. sugar to 0·756 water .	1 to 5·21
In 2 per cent. solution, 0·180 grm. sugar to 1·054 water .	1 to 5·85
In 5 per cent. solution, 0·459 grm. sugar to 2·405 water .	1 to 5·22
In 10 per cent. solution, 0·934 grm. sugar to 4·158 water .	1 to 4·43
In 20 per cent. solution, 1·430 grm. sugar to 6·672 water .	1 to 4·66

The mean of the various solutions is 1 part of sugar replaced by 5·07 water.

The phenomenon of the osmose of sugar partakes very much of a physical character, and may possibly prove to be nothing more than the exchange of sugar for water by the purely mechanical operation of diffusion.

A third series of observations on sugar were made in an osmometer of albuminated calico. The results, it will be seen, are quite in accordance with those of the membrane osmometers.

TABLE V.—Sugar in Osmometer F of Albuminated Calico for five hours.

I.	II.	III.	IV.	V.	VI.	VII.
Sugar in solution.	Rise in millimeter degrees.	Same in grammes of water.	Diffusate of sugar in grammes.	Previous maceration.	Hydrostatic resistance.	Temperature, Fahr.
per cent.				day.	min.	°
1	16	0·684	0·124	1	2	59
1	22	0·912	0·156	1	10	60
4	31	1·311	0·476	1	1	61
4	42	1·767	0·505	1	1	63
4	34	1·425	0·542	1	1	63
10	92	3·876	1·283	1	0·50	63
10	106	4·389	1·179	1	0·66	64
10	90	3·762	1·193	1	1	63

This osmometer is remarkable for the variable but generally very small amount of its hydrostatic resistance, a condition of the septum which is apt to increase the diffusate, owing to the expulsion of a portion of the solution by the pressure of the dense solution. The diffusates of sugar (Column IV.) may be considered as nearly proportional to the per-centage of sugar in the osmometer. The osmose of the 4 and 10 per cent solutions are also nearly proportional, the means being 36 and 96 ms.; but the osmose of the 1 per cent. solution is sensibly in excess. A slight excess in the early experiments with an albumen osmometer is, it may be remarked, not unusual, and appears to be due to the considerable quantity of soluble matter, with an alkaline reaction, which the fresh albumen affords to the water in the osmometer, this soluble matter then acting as an osmotic body.

Sulphate of Magnesia.—This salt was selected to illustrate the osmose of neutral salts. The sulphate of magnesia is neutral to test-paper. It appears, further, to be incapable of passing into the condition of a stable supersulphate or subsulphate by combining with an excess of either acid or base, and is not decomposed in diffusion. Such properties secure to a salt a remarkable indifference, or absence of chemical activity, and recommend sulphate of magnesia for our present purpose.

In a fresh double membrane, 1 per cent. of sulphate of magnesia (anhydrous) gave the small osmose of 13 and 14 ms., at 63°, in two experiments.

A full series of observations was made by means of the osmometer F, used above with sugar, but with the osmotic septum of course changed.

TABLE VI.—Sulphate of Magnesia in Osmometer F of double membrane for five hours.

I.	II.	III.	IV.	V.	VI.	VII.
Sulphate of magnesia (anhydrous).	Rise in millimeter degrees.	Same in grammes of water.	Diffusate of salt in grammes.	Previous maceration.	Hydrostatic resistance.	Temperature, Fahr.
per cent.				days.	min.	°
2	30	1·254	—	2	10	72
2	33	1·368	0·265	1	10	70
5	73	3·078	0·540	1	10	67
5	76	3·192	0·553	1	10	67
10	152	6·384	1·020	1	10	67
10	134	5·529	0·962	1	10	67
20	238	9·918	1·623	10	15	64
20	283	11·836	1·687	1	3·5	64
1	23	0·969	0·119	1	5	68
1	20	0·855	0·120	1	5	65
2	30	1·254	0·227	1	5	65
2	29	1·197	0·233	1	5	64
5	69	2·907	0·490	2	6	66
5	68	2·850	0·485	1	6	67
10	132	5·529	0·959	2	6	67
10	140	5·871	0·845	1	6	69
20	277	11·628	—	1	6	70
20	291	12·198	2·012	2	6	70

The diffusate increases in a somewhat less ratio than the proportion of salt in the osmometer in both of the two series of observations contained in the preceding Table. But a similar falling off in the amount of diffusate from the higher proportions of salt takes place in the diffusion of the same salt, from open phials, as appeared in former experiments on the diffusion of sulphate of magnesia.*

The different solutions then operated upon, and the ratio between the diffusates they gave, were as follows:—

Solutions of sulphate of magnesia diffused	2	4	8	16	24 per cent.
Ratio of diffusate of these solutions	2	3·671	6·701	11·785	15·678

The proportions of sulphate used in the present osmotic experiments were different, but ratios may be found for them by interpolation, and are given below. We are thus enabled to make the following comparison of the diffusion from different proportions of sulphate of magnesia: (1) in the absence of membrane; (2) in the first series of osmotic experiments given in the preceding Table; (3) in the second series of observations of the same Table:—

Sulphate of magnesia in solution	2	5	10	20 per cent.
(1) Ratio of diffusates without membrane	2	4·43	8·21	13·73
(2) Ratio of diffusates with membrane	2	4·12	7·48	12·5
(3) Ratio of diffusates with membrane	2	4·24	7·82	17·34

If the last number (17·34) given for the 20 per cent. solution of the later osmotic series be excluded, and it is manifestly in considerable excess from some accidental cause, the three sets of ratios must be allowed to exhibit considerable agreement.

The membrane appears to have a slight effect in reducing the diffusates of the higher proportions of salt; and this reduction is greater in the early experiments (2) than in the late experiments (3), made with the same osmometer. The comparative diffusion of different proportions of sulphate of magnesia appears, therefore, not to be much deranged by the intervention of membrane.

The average osmose of sulphate of magnesia likewise exhibits a pretty uniform progression. In the first series of experiments of Table VI., we find for the different proportions of salt in solution an osmose of 31·5, 74·5, 143, and 260·5 ms.; numbers which are in the ratio given below:—

Sulphate of magnesia in solution	2	5	10	20 per cent.
Ratio of osmose (first series of experiments)	2	4·73	9·08	16·54

In the later experiments of the same Table, the different proportions of salt (omitting the first and last proportions) give an average osmose of 29·5, 68·5, and 136 ms., of which the ratios may be stated as follows:

Sulphate of magnesia in solution	2	5	10 per cent.
Ratio of osmose (second series of experiments)	2	4·64	9·22

* Phil. Trans. 1850, p. 822.

The osmose appears here to follow more closely in its value the proportion of salt in solution than the diffusate can be said to do, either in open vessels or through membrane; so far, therefore, the osmose and diffusate do not preserve a constant proportion to each other with this salt.

No correction need be applied to the observed osmose of sulphate of magnesia, as this salt does not sensibly increase the bulk of the water in which it is dissolved. The weight of diffusate in Column IV. may, therefore, be immediately compared with the weights of water in Column III. It then appears that in the first series of the osmotic observations in the Table—

In 2 per cent. solution, 1 sulph. magnesia is replaced by 5.16 water.
 In 5 per cent. solution, 1 sulph. magnesia is replaced by 5.74 water.
 In 10 per cent. solution, 1 sulph. magnesia is replaced by 6.01 water.
 In 20 per cent. solution, 1 sulph. magnesia is replaced by 6.57 water.

According to the average of the whole proportions, sulphate of magnesia is replaced by 5.87 times its weight of water.

While in the later observations of the same Table—

In 2 per cent. solution, 1 sulph. magnesia is replaced by 5.33 water.
 In 5 per cent. solution, 1 sulph. magnesia is replaced by 5.9 water.
 In 10 per cent. solution, 1 sulph. magnesia is replaced by 6.32 water.

According to the average of the whole proportions of salt in these later observations, sulphate of magnesia is replaced by 5.85 times its weight of water.

The want of uniformity exhibited above in the relation between the quantities of water and salt goes some way to prove that the osmose of sulphate of magnesia in membrane is not pure diffusion, for the ratio between the exchanging water and salt (the *diffusion-volumes*) should then remain constant.

On the other hand, the approximation to uniformity favours the idea of the existence of a numerical relation between the osmose and diffusate. So also may the circumstance be considered, that sugar and sulphate of magnesia, which approximate, as seen above, in their osmose, were found before to have a similar degree of diffusibility.* The facts appear to afford a strong presumption, but no demonstrative proof, of the intervention of diffusion in governing the results of osmose in such neutral substances. The influence of diffusion becomes more difficult to trace in the osmose of three other neutral salts which I shall now introduce. What has been represented as the chemical agency now begins to interfere more sensibly, although not to govern the results entirely, as it appears to do in less strictly neutral salts.

Chloride of Sodium.—The osmose of chloride of sodium possesses a certain interest independently of such theoretical considerations.

* Phil. Trans. 1850, p. 10.

TABLE VII.—Chloride of Sodium in Osmometer C of double membrane for five hours.

I.	II.	III.	IV.	V.	VI.	VII.
Chloride of sodium.	Rise in millimeter degrees.	Same in grammes of water.	Diffusate of salt in grammes.	Previous maceration.	Hydrostatic resistance.	Temperature, Fahr.
per cent.				days.	min.	°
0.25	12	0.552	—	2	16	63
0.25	8	0.368	0.068	1	16	63
1	3	0.138	0.230	1	6	66
1	13	0.598	0.242	1	8	66
2	11	0.506	0.506	1	6	67
2	16	0.736	0.511	1	3	69
5	46	2.34	1.513	2	3	72
5	51	2.30	1.468	1	2	70
10	78	3.496	2.994	1	15	67
10	82	3.60	2.648	1	2	67
20	165	7.36	6.645	1	2	67
20	167	7.452	6.190	1	2	67

Chloride of sodium is known to diffuse with nearly double the rapidity of sulphate of magnesium in the smaller proportions of salt, and with a still higher velocity in the larger proportions of salt; accordingly the diffusates in the last Table exceed those of sulphate of magnesium in a corresponding ratio. The osmose appears pretty uniform, but with a tendency to fall below the average rate of the salt in the low proportions, such as 1 and 2 per cent., and to exceed the same rate in the higher proportions of salt. In a septum of single membrane, the osmose of a 10 per cent. solution was observed to rise to a high amount.

TABLE VIII.—Chloride of Sodium in Osmometer H of single membrane for five hours.

I.	II.	III.	IV.	V.	VI.	VII.
Salt in solution.	Rise in millimeter degrees.	Same in grammes of water.	Diffusate of salt in grammes.	Previous maceration.	Hydrostatic resistance.	Temperature, Fahr.
per cent.				day.	min.	°
2	21	1.04	0.917	1	16	66
2	24	1.20	0.955	1	16	68
10	272	13.28	6.502	1	16	68
10	311	15.68	7.850	1	12	68

An observation was made on the osmose of a high proportion of salt with another single membrane, differing from the last in offering considerably less hydrostatic resistance.

TABLE IX.—Chloride of Sodium in Osmometer I of single membrane for five hours.

I.	II.	III.	IV.	V.	VI.	VII.
Salt in solution.	Rise in millimeter degrees.	Same in grammes of water.	Diffusate of salt in grammes.	Previous maceration.	Hydrostatic resistance.	Temperature, Fahr.
per cent.				days.	min.	°
10	198	8.692	3.968	3	2.5	68
10	194	8.528	5.297	1	2.5	68

To these I add a series of observations of the osmose of the same salt in albumen, with the view of exhibiting the phenomenon in septa of that material. The well-preserved proportionality of the diffusate is remarkable.

TABLE X.—Chloride of Sodium in Osmometer K of albuminated calico for five hours.

I.	II.	III.	IV.	V.	VI.	VII.
Salt in solution.	Rise in millimeter degrees.	Same in grammes.	Diffusate in grammes.	Previous maceration.	Hydrostatic resistance.	Temperature, Fahr.
per cent.				days.	min.	°
1	16	—	0.141	4	8	65
1	27	—	0.219	1	8	62
4	39	—	—	1	2	60
4	34	—	0.625	3	2	56
10	43	—	1.580	1	3	59
10	61	—	1.615	1	3	60
10	72	—	1.597	1	3	61
1	27	—	0.153	1	2.5	63
1	22	—	0.141	2	4	63
0.1	27	—	0.016	1	2.5	63
0.1	20	—	0.018	1	4	64

Chloride of Barium.—Chloride of barium in its rate of diffusion from open vessels much resembles the chloride of sodium. Considerable analogy between the same salts is also observed in osmotic experiments.

TABLE XI.—Chloride of Barium in Osmometer L of double membrane for five hours.

I.	II.	III.	IV.	V.	VI.	VII.
Salt in solution.	Rise in millimeter degrees.	Same in grammes of water.	Diffusate in grammes.	Previous maceration.	Hydrostatic resistance.	Temperature, Fahr.
per cent.				days.	min.	°
2	35	1.476	—	2	10	72
2	45	1.886	0.675	1	10	70
5	94	3.936	1.706	1	8	67
5	111	4.674	1.640	1	6	67
5	74	3.116	1.203	1	10	67
10	154	6.478	4.491	1	10	67
10	133	5.576	3.395	10	16	64
10	136	5.74	2.929	1	4	64
20	267	11.214	6.860	1	8	68
20	283	11.79	7.030	1	8	65
1	60	2.542	0.275	1	8	65
1	74	3.116	0.230	1	8	64
5	74	3.116	0.602	2	8	66
5	74	3.116	1.587	1	8	67
10	152	6.396	3.795	2	8	67
10	154	6.478	4.040	1	8	69
20	337	14.186	—	1	8	70
20	320	13.448	8.130	1	8	70

TABLE XII.—Chloride of Calcium in Osmometer M of double membrane for five hours.

I.	II.	III.	IV.	V.	VI.	VII.
Salt in solution	Rise in millimeter degrees.	Same in grammes of water.	Diffusate in grammes.	Previous maceration.	Hydrostatic resistance.	Temperature, Fahr.
per cent.				days.	min.	°
2	6	0.258	—	2	8	72
2	6	0.258	0.795	1	8	70
6	45	1.935	2.29	1	8	67
5	60	2.64	1.83	1	3	67
5	51	2.24	2.636	1	8	67
10	228	9.92	4.256	1	8	67
10	188	8.24	3.607	10	12	64
10	176	7.76	3.11	1	6	64
20	380	17.2	6.075	1	3	68
20	398	17.6	—	1	3	65
2	24	1.04	0.668	1	4	65
2	27	1.2	0.625	1	4	64
5	81	3.6	1.512	2	5	66
5	83	3.68	1.467	1	5	67
10	185	8.16	3.158	2	5	67
10	181	8	3.317	1	5	69
20	406	18	6.695	1	5	70
20	416	18.4	6.992	1	5	70

Chloride of Calcium.—The diffusion of chloride of calcium in open vessels has been observed to fall below that of chloride of barium as 7·5 to 6·5.* But in membrane, judging from the following observations, the diffusion of chloride of calcium is the more rapid of the two. The osmose has also a tendency to rise, particularly in the larger proportions of chloride of calcium. The replacing water often exceeds twice the weight of the salt diffused. (See Table XII. p. 73.)

These three chlorides, possessing about double the diffusibility of sugar and sulphate of magnesia, should be replaced by half as much water as the latter substances. Some approach to this ratio may be perceived amid much irregularity in the observed osmose of the chlorides.

Proceeding now to the salts in which the osmose appearing to depend upon chemical properties preponderates greatly over osmose from diffusion, I may introduce these substances under the metals which they contain for the sake of their relations in composition.

POTASSIUM AND SODIUM.

Hydrate of Potash.—A highly intense osmose appears to be determined by caustic alkali, but it is necessary to apply the smallest proportions of alkali to avoid the rapid dissolution of the membrane. In double membrane 0·01 per cent. of hydrate of potash, or 1 alkali in 10,000 water, gave an osmose of 81 and 58 ms. By four times as much alkali, or 0·025 per cent., an osmose of 49 and 67 ms. was produced. These are the greatest effects.

On increasing the proportion of hydrate of potash to 0·5 per cent. the osmose sunk to 22 and 26 ms.; with 1 per cent. of hydrate of potash, to 13 ms. The permeability to hydrostatic pressure was always very great, being never less than one drop in a minute.

By the action of the alkali in the last experiment the permeability was increased from three to nine drops, and the membrane entirely ruined.

A similar experiment with hydrate of potash was made in albuminated calico with similar osmotic results. In the 0·01 per cent. solution an osmose of 76 and 58 ms. was observed; in 0·025 per cent. solution 87 and 126 ms.; in 0·5 per cent. solution 15 and 12 ms.; and in 1 per cent. solution—10ms., or a small negative osmose. The permeability both before and after the last experiment was represented by one drop in one minute; in both the half per cent. experiments the permeability was one drop in three minutes; in the preceding 0·025 per cent. solutions one drop in $2\frac{1}{2}$ minutes, and at the beginning one drop in ten and five minutes with the 0·01 per cent. solutions. The alkali first became sensible to the test-paper in the water-jar, in the diffusion of the 0·025 per cent. solutions. During both series of experiments the temperature ranged from 58° to 62°.

Carbonate of Potash.—The high osmose of this salt has already

* Phil. Trans. 1850, pp. 817, 819.

been often referred to in illustration of the influence of alkaline salts. The following experiments may be compared with those upon the neutral substances lately discussed, particularly in regard to their diffusates. They show also the comparative influence of membrane applied single and double to an osmometer.

TABLE XIII.—Carbonate of Potash in Osmometer B of single membrane for five hours.

I.	II.	III.	IV.	V.	VI.	VII.
Proportion of salt.	Rise in millimeter degrees.	Same in grammes of water.	Diffusate in grammes.	Previous maceration.	Hydrostatic resistance.	Temperature, Fahr.
per cent.				day.	min.	°
2	635	28.576	0.514	1	20	66
2	695	31.236	0.548	1	20	68
10	892	40.128	2.897	1	16	68
10	900	40.508	3.045	1	16	68

The fluid was removed from the water-jar at the expiration of the third hour, and replaced by distilled water to prevent the reaction of that portion of the salt which had already reached the jar upon the progress of diffusion from the osmometer, both in the preceding and the following series of experiments.

TABLE XIV.—Carbonate of Potash in Osmometer D of double membrane for five hours.

I.	II.	III.	IV.	V.	VI.	VII.
Proportion of salt.	Rise in millimeter degrees.	Same in grammes of water.	Diffusate in grammes.	Previous maceration.	Hydrostatic resistance.	Temperature, Fahr.
per cent.				day.	min.	°
2	449	21.883	0.324	1	16	66
2	484	23.621	0.400	1	16	68
10	619	30.178	2.764	1	16	68
10	595	28.993	3.150	1	12	68

In the double membrane, the average osmose of the 2 per cent. solution is reduced to 466 ms., from 665 ms. in the single membrane. The change is similar in the 10 per cent. solution, namely a reduction to 607 from 896 ms.; a reduction of nearly one-third of the osmose in the double membrane for both proportions of salt.

The difference of the diffusates is much less marked; for they

may be said to be the same for the 10 per cent. solutions, namely 2·966 grms. in the single, and 2·957 grms. in the double membrane; and for the 2 per cent. solution 0·531 grm. in the single, and 0·326 grm. in the double membrane. The diffusion of carbonate of potash, as seen here in membrane, will be found to correspond well with that of chloride of sodium (Table VII.), as the diffusion of the same two salts in open vessels is known to present a near approach to equality. The great osmose or current of fluid inwards might be supposed to diminish the outward movement of the salt under diffusion by washing back the salt into the osmometer. But the diffusates of the 10 per cent. solutions appear to have suffered no remarkable reduction from that or any other cause. The diffusate of carbonate of potash, which usually passes through membrane, appears, however, to be low. In the 1 per cent. solution, formerly referred to, it was 0·195 grm. In the series of observations likewise already referred to, the diffusate of carbonate was also low, but remarkably uniform, namely 0·018 grm. for 0·1 per cent. solution, 0·092 grm. for 0·5 per cent. solution, and 0·196 grm. for the 1 per cent. solution.

But these determinations were all made by the alkalimetric method, and when in subsequent observations the potash was also determined by weighing it as sulphate, the proportion of diffusate was found sensibly increased. It hence appears that carbonate of potash acts chemically upon the membrane, and that a portion of the alkali diffuses out in a neutralised state. Thus in five successive experiments with the 1 per cent. solution, in fresh double membrane, the diffusates by the alkalimetric method were 0·208, 0·254, 0·264, 0·215, and 0·189 grm. carbonate of potash; while the actual quantity of alkali found by direct analysis corresponded in the last four observations to 0·318, 0·353, 0·287, and 0·242 grm. The quantity of carbonate of potash which has suffered change in passing through the membrane is 0·064, 0·089, 0·072, and 0·053 grm. in these four experiments respectively.

The diffusates of carbonate of potash, increased by those quantities, approach too closely to those of chloride of sodium to warrant the supposition of any peculiar repression by membrane of the diffusion of carbonate of potash, which otherwise appeared probable.

The observations last commented upon belong to a number undertaken with the view of ascertaining three points of interest, which may excuse a fuller statement of the experiments. These points were, first, the influence upon osmose of the air dissolved in solutions of carbonate of potash, which might be supposed to take a part in the chemical action of the membrane; secondly, the effect of frequent repetition of the experiment in exhausting the osmotic activity of membrane; and, thirdly, the relation in osmose of an alkaline carbonate and phosphate.

TABLE XV.—Solutions in Osmometer L of double membrane for five hours.

Salt in osmometer.	Rise in millimeter degrees.	Temperature, Fahr.
Carbonate of potash, 1 per cent.	439	63
Same, deprived of air by boiling	376	64
Same, deprived of air by boiling	353	65
Same solution, unboiled	325	63
Same solution, unboiled	268	56
Phosphate of soda (2NaO HO PO_3) 1 per cent.	176	55
Same	194	58
Same, 0.1 per cent.	196	56
Same, 0.1 per cent.	190	58
Carbonate of potash, 0.1 per cent.	176	57
Same, 0.1 per cent.	227	65
Same, 1 per cent.	298	58
Same, 1 per cent.	335	64
Same, 1 per cent.	312	62

It will be remarked that the highest osmose (439 ms.) is obtained in the first experiment, and that the osmose falls off pretty regularly to the fifth experiment (268 ms.) The change in the aëration of the solution in the second and third experiments cannot be said to interfere with this progression. The influence of free oxygen on the membrane is not therefore indicated as a cause of osmose. It may be added, that the converse experiment of depriving the fluid of the water-jar of air by boiling, led also to a negative result. It will be remembered, further, that the osmose of oxalic acid was not interfered with by an addition of sulphurous acid, which was likely to counteract the action of oxygen, if such an action existed in osmose.

When phosphate of soda is substituted for carbonate of potash, both 1 per cent., the osmose declines from 268 to 176 ms. The phosphate of soda being repeated, the osmose rises a little, namely to 194 ms. The one-tenth per cent. solution of the same salt which follows, maintains here the considerable osmose of 196 and 190 ms. On returning again to the application of carbonate of potash in the instrument, the osmose gradually rises and regains 335 ms. for the 1 per cent. solution of that salt.

From these repetitions of osmose it may be inferred, that whatever be the nature of the chemical action on membrane which prompts osmose, that action is by no means of a rapidly exhaustible character.

It may be added, with regard to the osmotic action of extremely dilute solutions of carbonate of potash, that the osmose is lowered rapidly in proportions below one-tenth of a per cent. of that salt. The osmose of 0.01 per cent. of carbonate of potash, in double membrane, amounted only to 19, 23, and 17 ms. in three successive experi-

ments. The osmotic action of carbonate of potash must, therefore, be inferior to that of hydrate of potash in the extreme degrees of dilution.

In the experiments of the preceding series, the influence of a salt often appears not to terminate with its presence in the osmometer, but to extend to following experiments made with other salts, or made with different proportions of the original salt. If this arises from portions of the first salt remaining in the membrane, they must be portions which are not easily washed out. The substance of membrane may possibly have an attraction for highly osmotic salts, capable of withdrawing small quantities from solution. When the membrane, however, is removed from the osmometer, after such experiments as are referred to, slightly washed and then incinerated, only minute traces of the salt last used are commonly discovered; if, indeed, the salt has not entirely disappeared.

Phosphate and Carbonate of Soda.—The osmose of the carbonate of soda appears to be quite similar to that of carbonate of potash. A considerable amount of information respecting the two soda-salts named is conveyed in the following series of experiments, which include also observations on the serum of ox-blood.

TABLE XVI.— Solutions in Osmometer F of double membrane for five hours.

Salt in osmometer.	Rise in millimeter degrees.	Temperature, Fahr.
Phosphate of soda, 1 per cent.	382	63
Same, 1 per cent.	311	56
Same, 0·1 per cent.	205	55
Same, 0·1 per cent.	218	58
Carbonate of soda, 0·1 per cent.	294	56
Same, 0·1 per cent.	254	58
Same, 0·01 per cent.	50	57
Same, 0·01 per cent.	39	65
Same, 1 per cent.	306	58
Same, 1 per cent.	337	64
Phosphate of soda, 1 per cent.	193	62
Same, 1 per cent.	186	61
Serum of ox-blood, undiluted	39	59
Same	34	61
Same, diluted with equal vol. of water	31	61

The phosphate and carbonate of soda, when alternated in the same osmometer, show considerable steadiness in their respective rates of osmose.

The inferior osmotic quality of serum is remarkable, considering the alkalinity of that fluid. The loss of osmose in serum is due, I

believe, to the presence of chloride of sodium. The latter substance possesses an extraordinary power of reducing the osmose of alkaline salts, which was observed in a variety of circumstances, but which it will be sufficient to illustrate by the following series of experiments in an albumen osmometer.

TABLE XVII.—Solutions in Osmometer N of albuminated calico for five hours.

Salt in osmometer.	Rise in millimeter degrees.	Diffusate in grammes by analysis.	Same, by alkalimetry.	Previous maceration.	Hydrostatic resistance.	Temperature, Fahr.
				days.	min.	°
Carbonate of soda, 1 per cent.	139	0.157	0.092	1	3	57
Same, 1 per cent.	150	0.156	0.106	1	6	59
Same, 2 per cent.	141	—	0.242	1	6	65
Same, 4 per cent.	143	0.570	—	1	8	62
Same, 10 per cent.	204	1.562	1.450	1	12	60
Same, 10 per cent.	163	1.432	1.340	3	6	56
Same, 1 per cent.	138	0.216	0.147	1	6	59
Same, 1 per cent.	136	0.198	0.156	1	3	60
Same, 0.1 per cent.	188	—	0.005	1	10	61
Same, 0.1 per cent.	179	—	—	1	6	63
Carbonate of soda, 0.1 per cent. + chloride of soda, 1 per cent.	32	—	—	2	6	63
Same + same	36	—	—	1	6	63
Chloride of sodium, 1 per cent.	25	0.384	—	1	6	64
Same, 1 per cent.	18	0.325	—	1	3	65
Carbonate of soda, 1 per cent. + chloride of soda, 1 per cent.	69	—	—	1	5	63
Same + same	56	—	—	3	8	56
Carbonate of soda, 1 per cent.	157	0.190	0.164	1	6	55
Same, 1 per cent.	163	0.212	0.185	1	4	58
Same, 0.1 per cent.	152	—	—	1	20	56
Same, 0.1 per cent.	152	—	—	1	20	58

The osmose of the 0.1 per cent. solution of carbonate of soda is lowered, by the addition of 1 per cent. chloride of sodium, from 179 ms. to 32 ms. The osmose of 1 per cent. carbonate of soda, with the addition of an equal proportion of chloride of sodium, is 56 ms., and of 1 per cent. carbonate of soda alone, immediately following, 157 ms. The osmose of these mixtures appears to be assimilated to that of chloride of sodium itself, which comes out as 18 and 25 ms. in the same series of observations.

The rise of an alkaline liquid in the osmometer appears to be equally repressed by chloride of sodium, placed outside or dissolved in the fluid of the water-jar.

In illustration of this statement, I may adduce a short series of

observations made with fresh ox-bladder, having its thickness unreduced, which further show that the repressing power that appears in the chloride of sodium does not extend to two other substances, alcohol and sugar.

TABLE XVIII.—Solutions in Osmometer P of ox-bladder for five hours.

Salt in osmometer.	Rise in millimeter degrees.
Carbonate of potash, 0.25 per cent.	76
Same, 0.25 per cent.	96
Carbonate of potash, 1 per cent., against alcohol, 1 per cent., in jar	108
Same, 1 per cent., against sugar, 1 per cent., in jar	104
Same, 1 per cent., against chloride of sodium, 1 per cent., in jar .	18
Same, 1 per cent., against pure water in jar	114
Same, 1 per cent., against chloride of sodium, 1 per cent., in jar .	18
Carbonate of potash, 1 per cent. + chloride of sodium, 1 per cent., against water in jar	64
Carbonate of potash, 1 per cent., alone, against pure water in jar	134
Same repeated	114

Now another neutral salt, sulphate of potash, will be found to have the reverse effect upon the osmose of an alkaline carbonate, supporting and promoting the latter. Such results show how far we still are from a clear comprehension of the agencies at work in membranous osmose. Another property of chloride of sodium, equally singular, is, that the association of this salt (by itself so indifferent) with small proportions of hydrochloric acid, such as one-tenth per cent., determines a positive osmose in membrane, which is sometimes very considerable.

The osmotic action of the albuminated calico of Table XVII. is moderate in amount, but remarkably uniform. The small tenth per cent. solution assumes a pre-eminence in activity which is very curious. It was often observed in the inquiry, that the small proportions of active salts were more favoured in albuminated calico than in membrane; may it not thence be inferred that it is in the albumen plate that the chemical agency operates to most advantage?

Taking the mean diffusates of chloride of sodium and carbonate of soda from the lower part of the same Table, we have 0.354 chloride of sodium against 0.201 carbonate of soda, or 1 of the former to 0.568 of the latter. The diffusates of the same two salts, in open vessels, were more nearly in the proportion of 1 to 0.7. The comparative diffusion of carbonate of soda appears to be rather repressed than promoted by the septum.

The neutralisation of a portion of the alkaline salt during the os-

motie process is again indicated. The portion of carbonate of soda thus lost in the 1 per cent. solution appears to diminish on repetition of the experiment. At the head of the Table, the loss in two experiments is 0.065 and 0.050 grm. ; lower down, 0.069 and 0.042 grm. ; and near the bottom of the Table, 0.026 and 0.027 grm. The loss with the 10 per cent. solution is 0.110 and 0.092 grm., or not more than double the loss in the preceding 1 per cent. solutions of carbonate of soda.

Sulphates of Potash and Soda.—The sulphate of potash was made the subject of frequent experiment, with the view of obtaining light on the nature of osmose, at the commencement of the inquiry. But it is not well fitted for such a purpose, its action in the osmometer proving at first of a most perplexing character. With thick ox-bladder, sulphate of potash, dissolved in the proportion of 1 per cent., usually exhibited considerable osmose ; that is, about one-half of the osmose of carbonate of potash in similar circumstances. The osmose of the sulphate had, however, a peculiar disposition to increase in successive repetitions of the experiment with the same membrane. The osmose of this salt might also be doubled by allowing bladder in substance to macerate for some time in the solution before the osmotic experiment : soluble matter from the membrane manifestly influenced the result considerably in all experiments with sulphate of potash.

When the removal was effected of the muscular coat of bladder, the chief source of its soluble matter, the osmose of the salt in question fell greatly in amount instead of rising, like that of the carbonate of potash.

In the prepared membrane sulphate of potash presented a small moderate osmose, like chloride of sodium. But the salt must be exactly neutral to test-paper, and the membrane also free from foreign saline matter, otherwise very different results are obtained. In a double membrane, 1 per cent. of the neutral sulphate gave 21 and 20 ms. ; but the same solution, made alkaline by the addition of no more than one ten-thousandth part (0.01 per cent.) of carbonate of potash, started up to 101 and 167 ms., a much greater osmose than the proportion of carbonate of potash present gave afterwards by itself in the same membrane, namely, 19, 23 and 17 ms. The influence of the alkali is so persistent, that the membrane, macerated in water for a night after the last experiments, still gave 65 ms. with 1 per cent. of pure sulphate of potash.

The osmotic activity of sulphate of soda is equally excited by a trace of alkali, and both sulphates exhibit the same character in albumen as well as in membrane. This remarkable result of the combined action of the two salts is so likely to elucidate the chemical actions prevailing in osmose, that a fuller series of illustrative experiments may be recorded. The septum was of double calico, well albuminated, and presented a good resistance to hydrostatic pressure.

TABLE XIX.—Solutions in Osmometer Q of albuminated calico for five hours.

Salt in osmometer.	Rise in millimeter degrees.	Temperature, Fahr.
		°
Sulphate of potash, 1 per cent.	18	53
Same	21	57
Sulphate of potash, 1 per cent. + carbonate of potash, 0·01 per cent.	139	62
Same + same	81	56
Same + same	73	61
Same + carbonate of potash, 0·1 per cent.	254	61
Same + same	263	59
Carbonate of potash, 0·1 per cent., alone	92	57
Carbonate of potash, 0·1 per cent., alone	95	57
Sulphate of soda, 1 per cent. + carbonate of potash, 0·1 per cent.	257	62
Same + same	237	54
Same + carbonate of soda, 0·1 per cent.	299	54
Carbonate of soda, 0·1 per cent., alone	90	57
Same	127	58

The influence of the two alkaline carbonates in giving a high osmose to the sulphates, appears to be pretty nearly equal. The primary source of the great osmose may prove to be the action on membrane of the alkaline carbonates, which is promoted in some way by the presence of sulphate of potash, as it is retarded by the presence of chloride of sodium.

On the other hand, the moderate amount of osmose which appears to be proper to these sulphates is completely negatived by the most minute addition of a strong acid. Thus, 1 per cent. of sulphate of potash, with the addition of one ten-thousandth part (0·01 per cent.) of hydrochloric acid, had its osmose reduced, in the first experiment to 8 ms., and in the second experiment to -5 ms., the osmose becoming actually negative.

On one occasion, a specimen of well-crystallised sulphate of potash gave, when dissolved, a still more sensible negative osmose, namely -28 ms. On applying litmus to the solution, it was found to possess an acid reaction. But the addition of 0·01 per cent. carbonate of potash was sufficient to change the acid into an alkaline reaction, and to give rise to a positive osmose, amounting to 54 ms.

It occurred to me to macerate a fresh membrane in water, containing one-thousandth part (0·1 per cent.) of hydrochloric acid, for two days, before applying the membrane to the osmometer, and then to wash the membrane with distilled water till all acid reaction disappeared. With 1 per cent. of neutral sulphate of potash, this membrane gave in succession 17, 42, 35, and 62 ms.; with sulphate of soda, 1 per cent., following, 39, 25, and 25 ms.; and with sulphate of zinc (anhy-

drous), 1 per cent., after the last salt, 14 and 21 ms. These last results show a certain degree of unsteadiness in the osmose of the alkaline sulphates, probably arising from the osmose of these salts depending so much upon adventitious circumstances. The diffusates were carefully weighed, first when fully dried, at 212° , and again when ignited. The difference in the weighings arose from the presence of organic matter dissolved out of the membrane, of which it gives the quantity probably somewhat exaggerated.

First diffusate,	0.328 grm. sulphate potash.	
Second diffusate,	0.362 grm. sulphate potash,	0.019 organic matter.
Third diffusate,	0.351 grm. sulphate potash,	0.031 organic matter.
Fourth diffusate,	0.366 grm. sulphate potash,	0.025 organic matter.
Fifth diffusate,	0.356 grm. sulphate soda,	0.011 organic matter.
Sixth diffusate,	0.339 grm. sulphate soda,	0.019 organic matter.
Seventh diffusate,	0.334 grm. sulphate soda,	0.009 organic matter.
Eighth diffusate,	0.239 grm. sulphate zinc.	
Ninth diffusate,	0.260 grm. sulphate zinc.	

The diffusates of the two alkaline sulphates are remarkably uniform, the diffusate of sulphate of soda falling a little under that of sulphate of potash, but not so much as in open vessels. The diffusate of sulphate of zinc is still smaller, but relatively too high, as it should not much exceed one-half of that of sulphate of potash, judging from the diffusion of these salts in the absence of membrane. The organic matter accompanying the salt falls off in quantity in successive experiments, but continued to exist to the last, although it was not determined in the experiments with sulphate of zinc. The diameter of the disc of membrane was 123 millimeters, and its original weight, air-dried, 0.559 grm.

Oxalate of Potash, Chromate and Bichromate of Potash.—The only property of sulphate of potash which seems to be connected with the positive osmose of that salt, is its bibasicity as a sulphate. The alkaline character promotes positive osmose, and this character appears to be a distinction of polybasic salts. The common tribasic phosphate of soda is strongly alkaline to test-paper, and the bibasic pyrophosphate of soda enjoys the same property in a still higher degree. The sulphates of potash and soda are certainly neutral to test-paper, but they may be looked upon as potentially alkaline from the easy severation of the second equivalent of fixed base and its replacement by water, witnessed in all bibasic salts. In monobasic salts, on the contrary, a proclivity to the acid character may be suspected. Thus, although the chloride of potassium and nitrate of potash appear as neutral to test-paper as the sulphate of potash is, yet the chlorides and nitrates of the magnesian bases are more decidedly acid than their sulphates. It is just possible then, on this view, that the osmotic inferiority of chloride of sodium, and the power of that salt to counteract the positive osmose of carbonate of potash, may be exhibitions of acid character belonging to the former salt. The observations of the rise

in the osmometer of chloride of sodium, and also of the chlorides of barium and calcium, previously described, also have the appearance of being the effect of diffusion, modified by a slight chemical osmose of a negative character proper to these salts.

The polybasic constitution of oxalate of potash is well marked, and its positive osmose will be found below to be considerable, although the specimen of salt employed was strictly neutral to test-paper.

This salt also, like sulphate of potash, is shown not to counteract the high positive osmose of an alkaline carbonate.

The chromate of potash, although carefully purified by crystallisation, retained a slight alkaline reaction. On this account small additions were made to it of bichromate of potash in some experiments, but without materially diminishing the very sensible positive osmose of the former salt. A neutral chromate has of course the same bibasic character as a sulphate.

TABLE XX.—Oxalate and Chromate of Potash in Osmometer F of double membrane for five hours.

Solution of salt.	Rise in millimeter degrees.	Diffusate in grammes.	Previous macera- tion.	Hydro- static resistance.	Tempera- ture, Fahr.
			days.	min.	°
1 per cent. oxalate of potash . . .	164	—	1	11	65
Same	153	—	1	10	65
0·1 per cent. oxalate of potash . .	92	—	1	5	63
Same	90	—	2	6	61
1 per cent. oxalate of potash + 0·1 per cent. carbonate of potash . .	262	—	8	5	56
Same + same	337	—	1	5	60
0·1 per cent. carbonate of potash . .	322	—	1	3	62
Same	273	—	1	3	68
1 per cent. oxalate of potash + 0·1 per cent. carbonate of potash . .	294	—	1	3	62
Same + same	246	—	2	3	55
1 per cent. bichromate of potash . .	24	0·253	1	3	54
Same	19	0·318	2	1	56
1 per cent. chromate of potash . . .	109	0·326	1	1	62
Same	106	0·307	1	1	58
1 per cent. chromate of potash = 0·1 bichromate of potash	91	0·298	2	1	57
Same	79	0·281	1	1	60

The average rise for the 1 per cent. solution of each of the salts placed in the osmometer in a pure state is, bichromate of potash 21·5 ms., chromate of potash 107·5 ms., and oxalate of potash 158·5 ms. The average diffusate for the chromate of potash is 0·3165 grm., and for the bichromate of potash 0·2855 grm.

Like solutions were submitted to osmose at the same time in a septum of albumen for the sake of comparison with the preceding membrane osmometer.

TABLE XXI.—Oxalate and Chromates of Potash in Osmometer
K of albuminated calico.

Solution of salt.	Rise in millimeter degrees.	Diffusate in grammes.	Previous macera- tion.	Hydro- static resistance.	Tempera- ture, Fahr.
			days.	min.	°
1 per cent. oxalate of potash . . .	195	—	1	15	65
Same	173	—	1	15	65
0·1 per cent. oxalate of potash . . .	91	—	1	15	63
Same	100	—	2	20	60
1 per cent. oxalate of potash + 0·1 per cent. carbonate of potash . . .	161	—	8	15	56
Same + same	211	—	1	15	60
0·1 per cent. carbonate of potash . .	109	—	1	15	62
Same	120	—	1	15	68
1 per cent. oxalate of potash + 0·1 per cent. carbonate of potash . . .	195	—	1	15	62
Same + same	188	—	2	15	55
1 per cent. bichromate of potash . .	36	0·244	1	15	54
Same	34	—	2	10	56
1 per cent. chromate of potash . . .	129	0·253	1	10	62
Same	123	0·242	1	10	58
1 per cent. chromate of potash + 0·1 per cent. bichromate of potash . .	95	0·251	2	10	57
Same	102	0·320	1	10	60

The average rise for the 1 per cent. solution of each of the salts is, for bichromate of potash 35 ms., for chromate of potash 126 ms., and for oxalate of potash 184 ms., all a little higher than in the previous membrane osmometer. The diffusate is lower than before, probably owing to the less permeability of the albuminous septum, the weight of chromate of potash diffused being 0·2475 gramme, and of bichromate of potash 0·244 gramme.

The two chromates have been found to possess nearly equal diffusibility in open vessels, and to correspond closely in that property with sulphate of potash. The oxalate of potash exhibits a considerable osmose when present in the small proportion of one-thousandth part (0·1 per cent.), namely 91 ms. in membrane and 95·5 ms. in albumen. This is the surest indication of considerable osmotic capacity. Bin-oxalate of potash and free oxalic acid are both remarkable for high negative osmose.

Barium, Strontium, Calcium, Magnesium.—The salts of these metals never appear capable of producing strong positive osmose when dissolved in a proportion of less than 1 per cent. On the contrary, some of the salts of this class, particularly the nitrates, exhibit a tendency to negative osmose.

Hydrate of Baryta gave a small positive osmose for minute proportions of salt, which disappeared as the proportion of salt was increased, exhibiting an analogy in this respect to hydrate of potash. The results for hydrate of baryta in double membrane were 6, 4, 1,

and 1 degrees of osmose for the 0·1, 0·25, and 0·5 per cent. solutions. In albumen the same solutions gave 0, -8, -23, and -17 ms.; and the 1 per cent. solution gave -25 ms.

Hydrate of Lime exhibited similar characters to the last base. Undiluted lime-water gave in double membrane -20 ms. and -1 m.; while the same, diluted with four volumes of water, gave a positive osmose of 31 and 18 ms. In albumen the undiluted lime-water gave -48 and -30 ms.; the same, diluted with four volumes of water, gave 0 m. and 1 m.

Chloride of Strontium, 1 per cent., gave in double membrane 19, 27, and 26 ms.; following chloride of barium in the same membrane, 13 and 21 ms. Nitrate of baryta, in the same membrane, gave 12, 24, and 29 ms.; nitrate of strontia, following the latter, 27 and 31 ms.

Nitrate of Lime in membrane twice gave 19 ms., following chloride of calcium with 12 and 20 ms.; in albumen nitrate of lime gave 2 and 2 ms.

The 2 per cent. solution of the same salt in membrane gave only 6 and 6 ms. in two experiments.

Chloride of Magnesium gave in membrane -2 ms., and in albumen 6 ms., both experiments being made with the 1 per cent. solution, which is always to be understood when no particular percentage is stated.

Nitrate of Magnesia gave in membrane -24 and -20 ms. Both of these magnesian salts were prepared by saturating the acid with excess of magnesia. The tendency of monobasic salts of the magnesian class to chemical osmose of a negative character appears to be small in the salts of barium and strontium, to rise in those of calcium, and to culminate in the salts of magnesium itself.

Aluminium.—Nothing is more remarkable than the high positive osmose of certain salts of alumina. These salts emulate the alkaline carbonates in this respect. The property, too, appears to be characteristic of the sesquioxide type, and distinguishes the salts of sesquioxide of iron, sesquioxide of chromium, and the higher oxide of uranium, as well as alumina.

Sulphate of Alumina.—The sulphates of this type do not exhibit a high degree of osmose, although they are probably more osmotic than the magnesian sulphates as a class. Sulphate of alumina, 1 per cent., gave in membrane 57 and 67 ms., and for 0·1 per cent. 24 and 31 ms.

The diffusate was small, amounting in the second observation of the 1 per cent. solution to 0·033 gramme of tersulphate of alumina, together with an excess of 0·005 grm. of sulphuric acid, according to analysis.

Chloride of Aluminium, prepared by treating hydrochloric acid with an excess of hydrated alumina, was found by analysis to approach very nearly to the proportions of the definite compound Al_2Cl_3 . The following results with that salt were successively obtained in an osmometer of single membrane:—

With 1	per cent., rise of 540 ms. at 50° Fahr.
With 1	per cent., rise of 570 ms. at 49° „
With 1	per cent., rise of 450 ms. at 47° „
With 1	per cent., rise of 635 ms. at 49° „
With 0.1	per cent., rise of 510 ms. at 54° „
With 0.1	per cent., rise of 285 ms. at 48° „
With 0.1	per cent., rise of 410 ms. at 56° „

The numbers, which are all high, vary considerably among themselves, as often happens when osmose is intense and is observed in a single membrane. The temperatures of the water-jar are added in these and most other observations recorded, although it was difficult to draw any positive conclusion respecting the influence of heat upon the osmose of small proportions of salt. With large proportions of neutral salts, where diffusibility prevails, the osmose appeared to increase with the temperature, as does the proportion of salt diffused. With respect to the condition of the membrane used above, the first experiment was conducted in the membrane freshly dissected, and previous to any maceration or washing whatever, with a similar osmotic result, it will be observed, as in the later experiments made with the membrane after being repeatedly macerated.

In experiments of diffusing chloride of aluminium in open vessels, decomposition of that salt was observed with escape of free hydrochloric acid. The decomposition appeared, however, to affect much less of the chloride of aluminium than it does of the acetate of alumina.

In an albumen osmometer, chloride of aluminium gave an osmose of 245, 233, and 229 ms., at 57°, 58°, and 60°, with diffusates of 0.085, 0.123, and 0.095 gramme of salt, calculated from the quantity of chlorine found in the diffusate.

In the last experiment the solution was coloured with litmus, apparently without affecting the amount of osmose.

Acetate of Alumina was prepared by precipitating pure sulphate of alumina by means of the acetate of lead. Mr. Crum has shown that in this reaction one equivalent of acetic acid becomes free, and that the acetate of alumina produced has the form $\text{Al}_2\text{O}_3 + 2\text{C}_4\text{H}_3\text{O}_3$. A specimen of the pure binacetate, prepared by Mr. Crum, exhibited an equally high osmose as the salt mixed with free acid obtained by precipitation, which is used below.

TABLE XXII.—Acetate of Alumina in Osmometer G of double membrane for five hours.

Proportion of salt.	Rise in millimeter degrees.	Same in grammes of water.	Diffusate in grammes.	Previous maceration.	Hydrostatic resistance.	Temperature, Fahr.
per cent.				days.	min.	°
1	232	9.728	—	2	3.5	65
1	264	11.096	—	1	3.5	65
0.1	195	8.208	—	1	3.5	64
0.1	130	5.472	0.036	2	3	66
0.1	159	6.688	0.051	1	3	67
0.1	146	6.152	0.045	2	3	67

In the second and third experiments of the Table, the solutions were coloured distinctly blue, by means of the ordinary sulphate of indigo, without interfering much apparently with the osmose.

The diffusates, when given, are as binacetate of alumina, and were calculated from the alumina found in the water-jar.

In the last three observations of the one-tenth per cent. solution, the diffusate of salt is in proportion to the replacing water as 1 to 152, 131, and 137.

In osmometer F of single membrane, acetate of alumina gave a diffusate not exceeding one-third or one-fourth of the diffusate from sulphate of potash in similar circumstances. Thus, in three observations of the aluminous salt, the osmose was 356, 393, and 397 ms., with the corresponding diffusates of 0.102, 0.114, and 0.080 gramme of binacetate of alumina; while two experiments on sulphate of potash, which were intercalated between the second and third of the preceding observations, gave diffusates of 0.325 and 0.425 gramme of sulphate of potash.

The osmose of acetate of alumina does not appear to be sensibly affected by previous experiments made in the same membrane with sulphuric acid, but to fall greatly when an equal proportion of sulphate of potash is diffused along with the acetate of alumina. Of the following numbers, —4, 8, 7, 237, 7, and 18, the first three and the fifth, which are small, are the osmose of 0.1 per cent. sulphuric acid alone; the fourth, which is large, that of 1 per cent. of acetate of alumina, and the sixth that of 1 per cent. of acetate of alumina mixed with 1 per cent. of sulphate of potash, all in the same membrane. The diffusate of the pure acetate of alumina was 0.087 gramme, which is low for a 1 per cent. solution, as compared with the diffusates from the one-tenth per cent. solutions of sulphuric acid, which were 0.039, 0.042, 0.046, and 0.044 gramme of sulphuric acid.

The addition of an equal weight of chloride of sodium to the 1 per cent. solution of acetate of alumina, lowered the osmose of the latter salt, in osmometer F, from 397 to 267 ms. This is a small amount of interference compared with that exercised by the sulphate of potash in the same membrane.

Pure binacetate of alumina was found to be largely decomposed when diffused in open vessels, the acetic acid escaping and leaving behind the allotropic soluble alumina of Mr. Crum. This last substance is remarkable for its low diffusibility; but this subject will require further discussion on a future occasion.

Iron. Protosulphate of Iron.—This salt appeared, like sulphate of magnesia, to exhibit only the exchange by diffusion of one part of salt for five or six parts of water; the rise of fluid in the osmometer also increasing pretty uniformly with the proportion of salt. Thus, in double membrane of good resistance, 1 per cent. of this salt (always supposed anhydrous) gave 21 and 30 ms.; 4 per cent. 60 and 84 ms., at a temperature between 61° and 64° Fahr.

Protochloride of Iron.—This salt separates itself from some other magnesian chlorides, and gives rise to a positive chemical osmose, which is considerable in amount. To learn whether this arose from the passage of iron into the higher oxide or not, sulphurous acid and hydrosulphuric acid were mixed with the protochloride of iron; but, as will be seen below, without lessening the osmose.

TABLE XXIII.—One per cent. Solutions of several Magnesian Chlorides in Osmometer F of double membrane for five hours.

Salt in osmometer.	Rise in millimeter degrees.	Hydrostatic resistance.	Temperature, Fahr.
		min.	°
Chloride of magnesium	3	2	59
Chloride of zinc	48	2	61
Same	54	2	62
Chloride of manganese	24	1.75	62
Same	34	1.5	63
Protochloride of iron	160	1	61
Same	197	1	64
Same	435	2	65
Protochloride of iron + 0.1 per cent. sulphurous acid	404	4	62
Protochloride of iron, saturated with SH	332	4	64
Protochloride of iron, alone	155	4	61

The osmose of protochloride of iron is large, but singularly unsteady in amount, rising from 160 to 435 ms., and falling again to 155 ms.

In another double membrane, of rather small resistance (1 min.), the osmose of the same salt was only 94, 91, and 97 ms. Between the first and second of these experiments the membrane was washed with alcohol and ether, but without changing the character of the osmose. In experiments made with this last membrane, the 2 per cent. solution of protochloride of iron gave 151 and 157 ms.; and the 5 per cent. solution 189 ms.; or, the osmose did not rise in proportion to the quantity of salt in solution.

Nitrate of Sesquioxide of Iron, formed by saturating dilute nitric acid by hydrated sesquioxide of iron, gave, in single membrane, the high osmose of 322 and 359 ms. for 1 per cent. of salt; and 153, followed by 107 ms., for 0.1 per cent. of salt. The acetate of the same oxide gave, when a deep red colour, 207 ms., and when it had become nearly colourless, from the spontaneous precipitation of a portion of its oxide, 194 ms., or sensibly the same osmose.

Manganese.—Sulphate of manganese appeared to have no decided chemical osmose, giving in double membrane of moderate resistance (2 min.), for 1 per cent. of salt, 34, 51, and 50 ms.; for 4 per cent. of salt, 53 and 51 ms., and for 10 per cent. of salt, 57 and 59 ms. The low osmose of the larger proportions of this salt is exceptional, and would require confirmation.

The chloride of manganese has already been shown to be of low osmose in membrane (24 and 34 ms. Table XXIII.) ; in albumen the same salt gave 13 and 14 ms.

Cobalt.—The chloride of this metal appeared to possess no decided chemical osmose, 1 per cent. giving in double membrane 21 and 27 ms. ; 0.1 per cent. 20 and 23 ms., and 1 per cent. again 44 ms.

Nickel.—The sulphate of oxide of nickel resembled that of magnesia and protoxide of iron. In double membrane 1 per cent. gave 12 and 10 ms. ; 4 per cent. 38 and 38 ms. ; 10 per cent. 72 and 106 ms.

The chloride of nickel, however, appeared to have a tendency to chemical osmose, like the protochloride of iron, and gave in double membrane 52, 89, and 95 ms.

Zinc.—None of the salts of this metal can be said to exhibit decided chemical osmose ; sulphate of zinc giving 34 and 29 ms., nitrate of zinc 18 and 32 ms., and chloride of zinc 48 and 54 ms., all in double membrane.

Cadmium.—The nitrate of cadmium appeared to affect chemical osmose ; the 1 per cent. solution of this salt giving, in double membrane, 90, 124, and 137 ms.

Copper.—Copper appears to possess the capacity for chemical osmose in its salts generally, with the exception of the sulphate. But no sulphate appears to be remarkable for osmotic activity. The comparative osmose of four salts of copper in the same membrane is given below.

TABLE XXIV.—Solutions of 1 per cent. of Salts of Copper in Osmometer E of double membrane for five hours.

Salt in solution.	Rise in millimeter degrees.	Hydrostatic resistance.	Temperature Fahr.
		min.	°
Chloride of copper	351	1	60
Sulphate of copper	48	10	59
Nitrate of copper	154	10	60
Same	204	12	62
Acetate of copper	148	10	62
Same	102	10	63
Same	101	10	61

The rate of osmose is general a little deranged on passing from one salt to another in the same membrane, and in consequence the second or third experiment is always to be preferred to the first made with the same salt. The preferable numbers for the osmose of the preceding salts would therefore be, sulphate of copper 48 ms., acetate 102, nitrate 204, and chloride 351. The number for the sulphate, however, is probably too high, being raised by the previous chloride.

The salts of several of the magnesian metal exhibit a much lower osmose in albumen than in membrane. In an osmometer of the first

description nitrate of copper gave only 22 and 27 ms.; acetate of copper 22 and 25 ms., or no more osmose than is obtained from the corresponding salts of lime and magnesia.

Lead.—The salts of this metal are probably equally osmotic with those of copper. The nitrate and acetate of lead only were examined. The osmose of these two salts obtained in the same membrane was as follows :

TABLE XXV.—Solutions of 1 per cent. of Salts of Lead in Osmometer M of double membrane for five hours.

Salt in solution.	Rise in millimeter degrees.	Hydrostatic resistance.	Temperature Fahr.
		min.	°
Nitrate of lead	174	2	64
Same	211	2	65
Same	197	2	62
Acetate of lead	100	2	64
Same	97	2	61

The numbers which these results appear to authorise, were for acetate of lead 97 ms., and for nitrate of lead 204 ms. (mean of 211 and 197 ms.) The acetate exhibits, as usual, a considerably inferior osmose to the nitrate of the same base.

It appeared desirable to ascertain the osmose of higher proportions of a salt, which, like the nitrate of lead, exhibits decided osmose in the 1 per cent. solution. The first results appearing low, the membrane was washed with ether after the third experiment, a treatment of the membrane which in this instance sensibly improved its osmotic power.

TABLE XXVI.—Solutions of Nitrate of Lead in Osmometer K of double membrane for five hours.

Proportion of salt in solution.	Rise in millimeter degrees.	Same in grammes of water.	Diffusate in grammes.	Previous maceration.	Hydrostatic resistance.	Temperature, Fahr.
per cent.					min.	°
1	91	—	—	0	2	61
1	127	—	—	1	1	64
1	125	—	—	1	1	63
1	157	—	—	3	8	63
1	157	—	—	9	12	63
2	184	—	—	1	12	63
2	195	—	—	1	12	66
5	209	—	—	1	12	66
5	229	—	—	1	12	67
10	213	—	—	1	12	69
10	250	10.56	3.283	2	16	72

These experiments lead to the estimation of the osmose of nitrate of lead as follows:—in the 1 per cent. solution an osmose of 157 ms., in the 2 per cent. solution 195 ms., in the 5 per cent. solution 229 ms., and in the 10 per cent. solution 250 ms. This, it is to be observed, is but a small increase for the higher proportions of salt. The diffusate for the 10 per cent. solution of this salt may be considered of an average proportional amount. The replacing water then exceeds the salt diffused only about three and a half times.

It is curious that the hydrostatic resistance of the membrane increases so decidedly as the experiments advance, in the osmose of this and several other metallic salts, particularly nitrates. It is not to be supposed, however, that this change has any material influence upon the osmose.

Uranium.—The nitrate of uranium presented a high degree of osmose. This result scarcely affects the question of the constitution of the metallic oxide present in that salt, as a high osmose is exhibited, both by the salts containing an oxide of the type R_2O_3 , and by a portion at least of the class of protoxides. Viewed as an aluminous salt, the nitre of uranium has a basic composition ($Ur_2O_3 \cdot NO_5$), a circumstance which suggested the addition of free nitric acid to that salt in some experiments. The small proportion of one-tenth per cent. of nitric acid will be seen to have a moderate influence, and 1 per cent. of nitric acid to have an overpowering influence in reducing the extraordinary osmose of this salt.

TABLE XXVII.—Solutions of Nitrate of Uranium in Osmometer M of double membrane for five hours.

Proportion of salt in solution.	Rise in millimeter degrees.	Diffusate in grammes.	Previous maceration.	Hydrostatic resistance.	Temperature, Fahr.
			days.	min.	°
1 per cent. nitrate of uranium	288	0.078	1	1	60
1 per cent. nitrate of uranium	458	0.102	3	1	61
Same + 1 per cent. nitric acid	44	0.205	1	1	63
Same + same	70	0.136	1	3	66
Same + 0.1 per cent. nitric acid	304	0.078	1	3	62
Same + same	282	0.108	1	3	61

The inferior osmose of the first observation in the Table arose from the osmose of the early hours of the experiment being less than those of the later hours, the osmose for the five hours in succession being 36, 46, 67, 77, and 63 ms.

This progression, combined with the additional circumstance to be observed, that the diffusate is below the average in the same experiment, suggests the idea of an absorbing or retaining power in the membrane for the salt, which must first be satisfied before the osmose and diffusion can proceed in a regular manner.

The diffusate is throughout small, like that of an aluminous salt.

In an albumen osmometer the osmose of the same salt was inconsiderable, namely 49 and 53 ms.; but that osmose was not further reduced by the addition of nitric acid.

Tin.—The protochloride of tin exhibits a high degree of osmose, like so many other metallic protochlorides. The 1 per cent. solution gave in double membrane an osmose of 235, 253, 289, and 275 ms. The bichloride of tin following immediately in the same membrane gave only 27 ms. But the osmose of the bichloride of this metal is essentially negative, even when the salt is made as neutral in composition as possible. It has been already described.

Antimony.—The double tartrate of potash and antimony proved rather remarkable for low osmose.

In the first experiment with a double membrane the osmose of the salt in question was 38 ms., but the osmose fell in the second and third repetitions to 12 and 17 ms. The 4 per cent. solution of the same salt gave no more than 23 and 7 ms.

Mercury.—The osmose of the salts of both oxides of this metal is always positive, and generally considerable. The osmose appeared to be of least amount in the chloride (corrosive sublimate), to increase in the protonitrate, and to assume its greatest magnitude in the pernitrate. The first salt has a stability in solution which the latter two salts do not enjoy.

Extraordinary osmose is here, therefore, associated with facility of decomposition, as in so many other instances.

The influence of the presence of acids and of chloride of sodium upon the osmose of chloride of mercury was tried in the search for facts which might throw light on the osmotic process.

An acid in small proportion appears to favour, rather than otherwise, the osmose of chloride of mercury. Chloride of sodium, on the other hand, exerts its usual repressing influence upon the process.

TABLE XXVIII.—Solutions of Mercury in Osmometer C of double membrane for five hours.

Proportion of salt in solution.	Rise in millimeter degrees.	Previous macera- tion.	Hydro- static resistance.	Tempera- ture, Fahr.
		days.	min.	°
1 per cent. of chloride of mercury . .	116	4	4	60
Same	121	3	4	61
0.1 per cent. of chloride of mercury . .	62	1	4	63
Same	49	1	5	66
1 per cent. of chloride of mercury + 0.1 per cent. of hydrochloric acid	163	1	5	62
Same + same	132	1	4	61
Same + 0.1 per cent. of nitric acid . .	152	3	5	60
Same + same	122	1	2	59
Same + 0.5 per cent. of chloride of sodium	72	1	2	61
Same + same	60	1	1	62

Adopting the second experiments as the most trustworthy, we have for 1 per cent. of chloride of mercury an osmose of 121 ms., and for the same, associated with half its weight of chloride of sodium, 60 ms.

The osmose of chloride of mercury in albumen was very trifling, being only 5 and 9 ms.; chloride of mercury diffused in sensible quantity, however, through both the albumen and membrane.

Protonitrate of mercury gave, in double membrane, an osmose of 232, 346, and 350 ms.; in albumen much less, namely 47, 63, and 61 ms.

Pernitrate of mercury gave, in double membrane, 425 and 476 ms. for the 1 per cent. solution, and 296 ms. for the one-tenth per cent. solution, results which indicate osmotic power of the highest intensity.

The membrane preserved a considerable action after the last experiments, although macerated in water for a night, and imparted thereafter to a salt nearly neutral to osmose (nitrate of silver), a rise of 222 and 166 ms.

In albumen, pernitrate of mercury again was low, giving 32 and 54 ms. for 1 per cent. of the salt, and 34 and 46 ms. for the one-tenth per cent. solution.

Silver.—It is interesting to observe how this metal separates itself from mercury and the magnesian elements, and takes its place with the alkaline metals in the property of osmose, as in other chemical characters. Nitrate of silver appeared to possess a moderate positive osmose, like a salt of potash or soda. For the sake of comparison, the silver salt was followed by nitrate of soda in the experiments below.

TABLE XXIX.—Solutions in Osmometer G of double membrane for five hours.

Salt in osmometer.	Rise in millimeter degrees.	Previous maceration.	Hydrostatic resistance.	Temperature, Fahr.
		days.	min.	°
1 per cent. of nitrate of silver . . .	36	1	2	64
Same	34	1	2	65
0.1 per cent. of nitrate of silver . . .	27	1	2	62
Same	22	1	2	64
1 per cent. of nitrate of soda	7	2	2	61
Same	2	1	2	64

The experiments of the table indicate an average osmose of 35 ms. for 1 per cent. of nitrate of silver, and of 4.5 ms. for the same proportion of nitrate of soda. A considerable diffusate of silver appeared in all the experiments with the salt of that metal.

Gold and Platinum.—The chlorides of these metals have already been shown to possess a decided negative osmose, and in that respect to rank with acids.

In concluding this paper I may place together a series of numerical results which exhibit the osmose of substances of all classes. Some of these numbers have not been previously reported.

Osmose in membrane of 1 per cent. solutions expressed in millimeter degrees.

Oxalic acid	—148	Chloride of zinc	45
Hydrochloric acid (0.1 percent.)	—92	Chloride of nickel	88
Tetrachloride of gold	—54	Nitrate of lead	204
Bichloride of tin	—46	Nitrate of cadmium	137
Bichloride of platinum	—30	Nitrate of uranium	458
Nitrate of magnesia	—22	Nitrate of copper	204
Chloride of magnesium	—2	Chloride of copper	351
Chloride of sodium	+12	Protochloride of tin	289
Chloride of potassium	18	Protochloride of iron	435
Nitrate of soda	14	Chloride of mercury	121
Nitrate of silver	34	Protonitrate of mercury	350
Sulphate of potash	21 to 60	Pernitrate of mercury	476
Sulphate of magnesia	14	Acetate of sesquioxide of iron	194
Chloride of calcium	20	Acetate of alumina	393
Chloride of barium	31	Chloride of aluminum	540
Chloride of strontium	26	Phosphate of soda	311
Chloride of cobalt	26	Carbonate of potash	439
Chloride of manganese	34		

It will be observed that acid and alkaline salts are found at opposite ends of the series, or, while the acids possess negative osmose, the alkaline salts exhibit positive osmose in the highest degree. The remark will suggest itself, that in osmose water always appears to pass to the alkaline side of the membrane; as water also follows hydrogen and the alkali in the electrical endosmose.

The chemical action must be different on the substance of the membrane at its inner and outer surfaces to induce osmose; and according to the hypothetical view, which accords best with the phenomena, the action on the two sides is not unequal in degree only, but also different in kind. It appears as an alkaline action on the albuminous substance of the membrane at the inner surface, and as an acid action on the same substance at the outer surface. The most general empirical conclusion that can be drawn is, that the water always accumulates on the alkaline or basic side of the membrane.

The analogy does not fail even when the osmometer is charged with an acid solution and the osmose is negative. The stream is then outwards to the water, which is a basic body compared with the acid within the membrane.

The high positive osmose of the salts of the alumina type is exceedingly remarkable. The property is common to salts of alumina, sesquioxide of iron, sesquioxide of chromium, and the corresponding oxide of uranium. Now the property in these salts is small where the salt is stable, as in the sulphates, but becomes great where the affinity between the acid and base is comparatively weak, as in the chlorides, nitrates, and acetates of these bases, salts which can be shown to be largely decomposed in the experiment by the action of diffusion. Here then, as with the preceding class of osmotic bodies, the osmose of the water is towards the basic side of the membrane.

But the most curious circumstance, with reference to this empirical

generalisation, is observed in the magnesian class of salts. The barytic subdivision of this class, including all the soluble salts of baryta, strontia, and lime, appear to be entirely unosmotic, or they oscillate between a small positive and small negative osmose. Such salts are neutral in their reaction, and further, have no disposition whatever to form subsalts. The salts of the earth, magnesia itself, offer the same characters. But in the salts of certain other oxides of the magnesian group an intensely osmotic character is developed, particularly in the salts of copper, protoxide of lead and protoxide of tin, with the exception of the soluble sulphates of these bases. Now those named are the members of the magnesian class most apt to break up into free acid and a basic salt. Like the aluminous salts, therefore, they are capable of investing the inner surface of the membrane with basicity, the necessary condition of positive osmose. Nitrate of uranium does not require to form a subsalt, as it is already constitutionally basic. The osmotic peculiarity of metaphosphoric acid, formerly referred to, also harmonises with the same view.

Neutral monobasic salts of the alkaline metals, such as the chlorides of potassium and sodium, and the nitrates of potash, soda, and silver, which possess a strict and unalterable neutrality, appear to have little or no true osmotic action. The salts named, together with the neutral magnesian sulphates and certain neutral organic substances, such as alcohol and sugar, give occasion, it is true, to an increase in the fluid of the osmometer, but only to the moderate extent which the exchange of diffusion-volumes might be supposed to produce. The comparative diffusibility of all these substances is well known, with the exception, unfortunately, of that of water itself, which I could only deduce by an indirect method in my previous inquiries respecting liquid diffusion. As salts generally appeared to diffuse in water four times more rapidly than they did in alcohol, the diffusibility of water was then assumed as probably four times greater than that of alcohol, and consequently five or six times greater than that of sugar or sulphate of magnesia. Diffusion is thus made to account for the substances last named being replaced in the osmometer by five or six times their weight of water. This "diffusion-osmose" appears to follow in its amount the proportion of salt in solution, with a certain degree of regularity. The "chemical osmose" of substances, on the other hand, is found of high intensity with small quantities of the substance, such as 1 per cent. or even 0.1 per cent., and to augment very slowly with increased proportions of the substance in solution.

A small proportion of common salt accompanying carbonate of potash has been seen to possess a singular influence in diminishing the positive osmose of the last-named alkaline salt; while a mixture of small proportions of common salt and hydrochloric acid exhibits, with the membrane in certain conditions, an intense positive osmose which neither of these substances possesses individually.

The bibasic salts of potash, again, such as the sulphate and oxalate,

although strictly neutral in reaction, begin to exhibit a positive osmotic power, in consequence, it may be supposed, of their resolvability into an acid salt and free alkaline base.

The sulphate of potash, when strictly neutral, has in different membranes a variable but always moderate positive osmose, an osmose which the slightest trace of a strong acid may cause to disappear entirely, or even convert into a small negative osmose.

On the other hand, a minute addition of an alkaline carbonate to the sulphate of potash appears to give that salt a positive osmose of a high order. It was seen that the mixed salts produce much more osmose than the sum of the osmose of the two salts used apart from each other.

It may appear to some that the chemical character which has been assigned to osmose takes away from the physiological interest of the subject, in so far as the decomposition of the membrane may appear to be incompatible with vital conditions, and osmotic movement confined therefore to dead matter. But such apprehensions are, it is believed, groundless, or at all events premature. All parts of living structures are allowed to be in a state of incessant change,—of decomposition and renewal. The decomposition occurring in a living membrane, while effecting osmotic propulsion, may possibly therefore be of a reparable kind. In other respects chemical osmose appears to be an agency particularly well adapted to take part in the animal œconomy. It is seen that osmose is peculiarly excited by dilute saline solutions, such as the animal juices really are, and that the alkaline or acid property which these fluids always possess is another most favourable condition for their action on membrane. The natural excitation of osmose in the substance of the membranes or cell-walls dividing such fluids seems therefore almost inevitable.

In osmose there is, further, a remarkably direct substitution of one of the great forces of nature by its equivalent in another force—the conversion, as it may be said, of chemical affinity into mechanical power. Now, what is more wanted in the theory of animal functions than a mechanism for obtaining motive power from chemical decomposition as it occurs in the tissues? In minute microscopic cells the osmotic movements should attain the highest velocity, being entirely dependent upon extent of surface. May it not be hoped, therefore, to find in the osmotic injection of fluids the deficient link which intervenes between chemical decomposition and muscular contraction?

The intervention of the osmotic force is also to be looked for in the ascent of the sap of plants. The osmometer of albuminated calico appears to typify the vegetable cell; the ligneous matter of the latter being the support of a film or septum of albuminous matter, in which the active properties of the cell reside. With a vegetable salt, like oxalate of potash above, and pure water below such a septum, an upward movement of the lower fluid would necessarily ensue.

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VII.—*Chemical Composition of the Waters of the Metropolis
during the Autumn and Winter of 1854.*

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THE important bearing of the composition of the waters supplied to the inhabitants of the metropolis on the public health, may serve as a sufficient apology for the addition of another to the many previous investigations which have been instituted on this subject. The valuable report communicated to this Society in 1851, details researches which were made under particular circumstances during the winter season, and at a time when the diluting influence of recent rain had tended to modify the constitution of the metropolitan waters. In the present paper it is intended to comprise a summary of an extensive series of analyses which were made from the 1st of September, 1854, to the beginning of the present year. From these results it is apparent that the waters supplied to London possess in many respects a fluctuating character, which may tend in some measure to explain the antagonistic views that have at different times been entertained with regard to their adaptation to domestic purposes.

In order to determine the composition of the waters as supplied to the inhabitants, specimens of water were taken from houses generally in which the epidemic had proved fatal, and these were compared,

when the object could be conveniently accomplished, with samples obtained from the sources of supply.

In the course of the inquiry it was observed that the composition of the Chelsea and Southwark Companies' waters depended so much on the state of the river under different circumstances, that it was found necessary to examine the Thames at various periods of the tidal flow, so as to obtain a basis for the explanation of remarkable apparent discrepancies. The following table gives the composition of the river in different parts of its course at high and low waters, the Vauxhall samples having been obtained at a point intermediate between those from which the Chelsea and Southwark Companies derive their supply. The amounts are stated in grains per gallon, convertible into degrees of impurity.*

TABLE I.
High Water.

	Vauxhall.	Hungerford.	London Bridge.	Greenwich.
Mechanical impurity . .	60°50	64°64	63°44	—
Organic impurity . .	5·28	5·80	4·72	—
Inorganic impurity . .	36·64	45·24	45·08	—
Total impurity . .	102·42	115·68	113·24	—
Chlorine	22·00	24·00	24·00	—

Low Water.

Mechanical impurity . .	10·26	16·80	3·52	3·70
Organic impurity . .	4·34	8·40	7·36	19·44
Inorganic impurity . .	12·54	23·64	21·20	72·54
	27·14	48·84	32·08	95·68

In collecting these specimens, care was taken that each series should be obtained on the same day, and as nearly as possible at each locality at the corresponding periods of the tide.

When this table is compared with that which now follows, the varying composition of the Thames waters, taken from the lower portion of the river's course, obviously depends on the chemical state

* I have proposed, in concurrence with the opinion of some eminent engineers of water-works, to designate pure distilled water by 0, and to express by degrees equivalent to grains per gallon the mechanical and soluble matters contained in water.

of the water in the river as affected by the tidal flow at the period when the Company's engines are in action.

TABLE II.
Total Residue in Thames Waters.

		Grains per Imperial Gallon.				
		Lambeth Company.	Grand Junction Company.	West Middlesex Company.	Chelsea Company.	Southwark Company.
August, 1854	.	—	—	—	—	56·26
September, "	.	13·37	14·42	19·04	60·17	48·18
October, "	.	—	—	—	—	43·50
November, "	.	17·40	17·92	18·97	—	41·78
December, "	.	—	—	—	36·96	—
March, 1855	.	—	—	—	—	23·15

According to these data, which are the means of many experiments, the Southwark and Vauxhall water is more than twice as impure in August as in March. These numbers, however, do not convey a correct idea of the highest extreme obtained, since in September the water has been found to contain 72·66 grains per gallon on one occasion in Walworth. A similar observation applies to the water of the Chelsea Company. But it will be observed that the higher sources of supply from the river afford the purest water during the dry seasons, and the largest amount of matter in solution during the wet seasons, as the rains bring down the soluble constituents of the soil from the agricultural districts, and add to the total amount both of earthy and alkaline salts. In the following series, the analyses are divided into two groups, Tables III. and IV., the first comprising the Thames waters, and the second those obtained from other sources. The total water supplied to the metropolis by the various companies in 1853, amounted to 60,614,420 gallons, of which 28,638,576 gallons were derived from the Thames. Considerable modifications in these works have been introduced by some of the water companies within a recent period, which have contributed to improve the quality of the waters. Thus, the Lambeth Company's water is now obtained from Thames Ditton, while important new cuttings have been made by the East London Company, so as to avoid the influence of contaminating sewage. As the object in view in making the present investigation, was to determine the nature of the water as used in the

several localities from which the samples were taken, the specimens were usually collected from the cisterns, if possible, at the time when the service-pipe was delivering the supply. This may account for some differences in the amount of carbonate of lime, which is well known to precipitate to some extent by exposure.

In all the waters collected during the course of the inquiry, abundance of animal and vegetable life was detected in mechanical suspension, and although the experiments were in some measure in abeyance before the cold weather set in, remarkable examples were incidentally noticed, during the severest frost, of the persistence of vitality among some of the larger animal forms familiar to those who have microscopically examined the Southwark water. The fibrine of the *fæces* has also constantly been obtained from service-pipes of the Southwark Company,—a fact which has led to further investigation in reference to the presence of other products of animal origin in the Lambeth and Southwark waters, these two waters being derived from the two extremes of the river, so far as the Thames Companies are involved. The results of these inquiries are included in Table III., under the head of carbonate of ammonia, and under Table V. As the waters from Thames Ditton and from the Thames at Vauxhall were tested for ammonia on the same day, the difference in the amount of ammonia in favour of Vauxhall water is obviously due to the influence of human excretions. And it would also appear from experiments on other rivers not subject to the reception of sewage, that the Thames Ditton water is supplied with an excess of ammonia due to the influence of different sources of pollution. In a chemical paper no attempt to discuss the nature of the organised matter diffused through the waters has been made. The analyses were made from quantities of the residual ash obtained by evaporation.

TABLES III. and IV.

Composition of Metropolitan Waters.

	Grains per Imperial Gallon.							
	Thames Waters.					Other Waters.		
	I.	II.	III.	IV.	V.	I.	II.	III.
	Lambeth Company.	Grand Junction Company.	West Middlesex Company.	Chelsea Company.	Southwark Company.	New River Company.	East London Company.	Kent Company.
Organic matter.....	1.390	1.920	2.080	5.410	3.560	2.330	1.940	1.480
Silica.....	.350	.090	.520	1.511	.240	.180	.320	.420
Sesquioxides of iron, alumina, and phosphates.	.215	.730	.460	.639	.460	.400	.520	.130
Insoluble lime.....	5.680	4.967	5.555	5.348	5.992	6.712	6.718	5.342
Soluble lime.....	.944	.975	.868	2.649	2.374	.918	.549	1.254
Insoluble magnesia.....	.281	.343	.342	.209	.238	.407	.354	.100
Soluble magnesia.....	.200	.228	.157	1.283	.886	trace	.100	.400
Sodium.....	.379	.372	.643	11.708	5.967	.942	9.951	.343
Potassium.....	.328	.249	.259	1.304	1.086	.320	.307	.518
Ammonia.....	.023	—	—	—	.297	—	—	—
Sulphuric acid.....	1.599	1.647	1.504	6.043	2.980	1.393	.841	2.344
Chlorine.....	1.020	0.980	1.160	19.554	12.160	1.430	.860	1.240
Nitric acid.....	—	—	—	—	.050	—	—	—
Carbonic acid.....	9.550	8.560	9.880	9.106	9.941	11.442	11.336	8.616
<hr/>								
Organic matter.....	1.390	1.920	2.080	5.410	3.560	2.330	1.940	1.480
Silica.....	.350	.090	.520	1.511	.240	.180	.320	.420
Sesquioxide of iron, alumina, and phosphates.	.215	.730	.460	.639	.460	.400	.520	.130
Carbonate of lime.....	10.144	8.870	9.919	9.550	10.700	11.985	11.997	9.540
Sulphate of lime.....	2.149	2.363	2.109	6.432	3.179	1.812	.897	3.085
Nitrate of lime.....	trace	trace	trace	trace	.076	trace	trace	trace
Chloride of calcium.....	—	—	—	—	2.108	—	—	—
Carbonate of magnesia.....	.592	.720	.720	.438	.500	.855	.743	.210
Sulphate of magnesia.....	—	—	—	1.390	—	—	—	—
Chloride of magnesium.....	.617	.542	.360	1.947	2.101	trace	.237	.949
Sulphate of potash.....	.730	.553	.577	2.903	2.413	.712	.682	1.153
Chloride of potassium.....	—	—	—	—	trace	—	—	—
Sulphate of soda.....	—	—	—	trace	trace	—	—	—
Carbonate of soda.....	—	—	—	—	trace	—	—	—
Chloride of sodium.....	.966	.947	1.637	29.797	16.001	2.355	1.125	.874
Total.....	17.153	16.740	18.443	60.017	40.593	20.629	18.461	17.841
Residue by evaporation.....	17.440	16.920	18.970	60.170	41.780	20.780	18.300	17.760
Carbonate of ammonia.....	.061	—	—	—	.840	—	—	—
Hardness.....	13.2	12.6	12.8	18.4	18.2	14	14.2	12.2

AMMONIA IN THE LAMBETH AND SOUTHWARK COMPANIES' WATERS.

As the absolute and relative amount of ammonia present in water, in addition to the quantity of nitric acid, is a question of vital importance in regard to the sources of the contaminating influences to which waters are subjected, it seemed desirable to make the experiments upon such a scale of magnitude, that minor difficulties occurring on the small scale of operations might be obviated. In the subsequent tables, exhibiting the amount of ammonia present in Southwark water, the quantity operated on was always 50 gallons, which were introduced into a copper still, and boiled for a considerable time in order to precipitate the carbonate of lime. About 2 gallons of distilled water were usually drawn off, and were never found alkaline; from which it might be inferred that no carbonate of ammonia existed in the water: but the distillation was scarcely protracted sufficiently long to decide this question. About half a pint of strong caustic soda was then poured into the boiler, and the 2 gallons of distilled water returned. When the amount of ammonia present in the water was considerable, the distilled fluid gave evidence of an alkaline reaction in about two minutes after the addition of the soda, which accounts for the facts exhibited in the table, of the largest amount of ammonia being found to exist in the second half gallon, as in Nos. 1 and 2. When the quantity of ammonia was feeble, as in No. 4, no alkalinity was detected till the fourth half gallon was distilled. The rate at which the ammonia distilled was found to depend, in a great measure, on the mode of the application of the heat to the still, the higher the temperature the more rapid being the evolution of the ammonia, as in Nos. 1 and 2; while in No. 5, the gradual application of the heat caused the alkalinity to be appreciable even in the eighteenth half-gallon of distilled water.

The alkalinity was neutralised in all the experiments in the table by sulphuric acid diluted to such a degree, that 100 alkalimeter measures saturated 38.46 of soda, or 21.112 of ammonia. Each 100 measures, therefore, contained 49.67 parts of sulphuric acid. In order to check the numbers determined by the neutralising acid, the whole of the fluids, after the addition of a slight excess of acid, were evaporated to dryness, and the residual sulphate of ammonia, freed from a small portion of lime with which it was usually contaminated, dried cautiously in a dry atmosphere and weighed. The controlling numbers thus obtained are exhibited in Table VI. Generally they exceed the quantity procured by means of the acid process, because several additional gallons which were drawn off, although destitute of

any appreciable alkalinity, were acidified and boiled down to obtain their residue, which was added to the rest of the sulphate. The Southwark and Vauxhall water was examined on this extensive scale, because the operation could be conveniently performed; but in the case of the Lambeth water, as the fluid required to be brought from a distance, the distillation was made with 10 gallons; acid was added to the distillate until the reaction indicated an excess; the water was cautiously evaporated; and the ammonia determined as platino-sal-ammoniac. In the case of the St. Thomas's Well, the amount distilled from was 50 gallons.

TABLE V.

Southwark.

Half-Gallons.	Measures of Acid.					St. Thomas's Well.
	I. Nov. 30, 1854.	II. Dec. 22, 1854.	III. January 5, 1855.	IV. March 17, 1855.	V. March 17, 1855.	
1st	8.5	11.0	6.0	0.0	8.0	
2d	11.5	13.0	6.0	0.0	6.0	
3d	6.0	9.0	4.0	0.0	6.0	
4th	5.5	7.0	4.0	2.0	5.0	
5th	5.5	6.0	4.0	1.5	4.0	
6th	5.5	6.0	4.0	1.5	3.5	
7th	5.5	5.0	5.0	1.0	3.5	
8th	—	4.0	5.0	1.0	3.0	
9th	—	4.0	2.0	1.0	3.0	
10th	—	3.0	0.0	1.0	2.5	
11th	—	2.5	0.0	0.5	2.0	
12th	—	—	0.0	0.5	2.5	
13th	—	—	—	—	2.0	
14th	—	—	—	—	1.5	
15th	—	—	—	—	1.0	
16th	—	—	—	—	1.0	
17th	—	—	—	—	0.5	
18th	—	—	—	—	0.5	
	48.0	70.5	40.0	10.0	55.5	

TABLE VI.

Amount of Ammonia in Southwark and Lambeth Waters.

	Nov. 30 1854.	Dec. 22, 1854.	Jan. 5, 1855.	Mar. 17 1855.	St. Tho. Well. Mar. 17 1855.
Southwark and Vauxhall Water, and St. Thomas's Well:—					
Ammonia (NH_3) in 50 gallons, deter- mined by an acid	10.134	14.884	8.444	2.111	11.717
Ditto, by evaporation as sulphate	—	—	—	2.575	11.874
Ammonia (NH_3) per gallon, determined by acid203	.298	.169	.042	.234
Ditto, by evaporation as sulphate	—	—	—	.0515	.2375
Carbonate of ammonia ($\text{NH}_3\text{CO}_2\text{HO}$), per gallon573	.850	.477	.119	.661
Lambeth Water Company:—					
Ammonia, per 10 gallons2290	—	—	—	—
Ditto, 1 gallon0229	—	—	—	—
Carbonate of ammonia, per gallon0640	—	—	—	—

SOFTENING PROCESS FOR WATERS.

Having had an opportunity of witnessing on an extended scale at Plumstead, under the management of Mr. Homersham, the efficiency of Dr. Clark's softening process, it may be satisfactory to subjoin analyses of two chalk-waters in their natural and softened conditions:—

	Watford.		Plumstead.	
	Hard.	Soft.	Hard.	Soft.
Organic matter	1.400	1.420	2.720	2.800
Silica480	.680	.720	.720
Alumina and phosphates240	.120	.340	.280
Carbonate of lime	14.131	.520	11.406	.400
Carbonate of magnesia870	.390	1.450	.400
Sulphate of lime	1.887	.500	8.864	8.076
Nitrate of lime	1.521	1.580	—	—
Sulphate of potash569	.569	.284	.284
Sulphate of soda	—	—	1.235	1.445
Chloride of sodium	1.153	1.548	3.558	3.054
Total	22.251	7.327	30.577	18.359
Residue by evaporation	22.400	8.030	30.900	18.28

These data are sufficient, if any were required, to demonstrate that practically the softening process is as successful as theory would indicate.

VIII.—*On Platinised Charcoal.*

By DR. JOHN STENHOUSE, LL.D., F.R.S.

THE lighter kinds of wood charcoal, owing to the nine volumes of oxygen gas contained in their pores, possess a considerable power of oxidising the greater number of easily alterable gases and vapours. The absorbent power of charcoal, however, is comparatively much greater than its capacity for inducing chemical combination. In this respect, charcoal presents a remarkable contrast to spongy platinum, which, though inferior as an absorbent for some gaseous substances,—such for instance as ammonia, of which spongy platinum absorbs only 30 volumes, while charcoal absorbs 90,—is, nevertheless, immensely more effective, both as an oxidiser, and as a promoter of chemical combination generally. As it is desirable for some purposes, while retaining the absorbent power of charcoal unimpaired, to increase its oxidating influences, it struck me that this important object might be easily effected by combining the charcoal with minutely divided platinum. In this way, a combination is produced to which I have given the name of platinised charcoal, which possesses the good properties of both of its constituents. In order to platinise charcoal, nothing more is necessary than to boil the charcoal, either in coarse powder or in large pieces, in a solution of bichloride of platinum, and when the charcoal has become thoroughly impregnated with the platinum, which seldom requires more than ten minutes or a quarter of an hour, to heat it to redness in a close vessel—a capacious platinum crucible being very well adapted for this purpose. When 150 grains of charcoal were impregnated with nine grains of platinum, by the process just described, the charcoal was found to have undergone no change in its external appearance, though its properties had been very essentially altered. When a few grains of this platinised charcoal were passed up into a mixture of dry oxygen and hydrogen in the proportions to form water, over mercury, the two gases rapidly combined in the course of a few minutes, precisely in the same way as when a clay ball of spongy platinum is employed. When, however, a fragment of charcoal containing a considerably larger proportion of platinum was passed up into a similar gaseous mixture, the gases instantly combined with explosive violence, just as if platinum-black had been used. If pieces of cold platinised charcoal are held in a jet of hydrogen, they speedily become incandescent, and inflame the gas. Platinised charcoal, when slightly warmed, likewise rapidly

becomes incandescent in a current of coal gas, but the jet of gas is not inflamed, owing to the very high temperature, a white heat, which is required for this purpose.

In the vapour of alcohol or wood-spirit, platinised charcoal becomes red hot, and continues so till the supply of vapour is exhausted. In the course of a few hours, spirits of wine, in contact with platinised charcoal and air, is converted into vinegar. I find that two per cent. of platinum is sufficient to platinise charcoal for most purposes. Charcoal containing this small amount of platinum causes a mixture of oxygen and hydrogen to combine perfectly in about a quarter of an hour, and this is the strength of platinised charcoal that seems best adapted for charcoal disinfectant respirators. Charcoal containing one per cent. of platinum causes a mixture of oxygen and hydrogen to combine in about two hours; and charcoal containing the extremely minute quantity of $\frac{1}{4}$ per cent. platinum, produces the same effect in from 6 to 8 hours. Platinised charcoal seems likely to admit of various useful applications: one of the most obvious of these is its excellent adaptability to air-filters and respirators for disinfectant purposes. It is plain that no easily alterable organic vapours, such as effluvia or miasmata, can remain in contact, even for a few minutes, with platinised charcoal, without being destroyed, their carbon being converted into carbonic acid and their hydrogen into water.

Platinised charcoal also seems likely to prove a highly useful application to malignant ulcers and similar sores, on which I confidently expect, from its powerful oxidating properties, that it will act as a mild but effective caustic. Perhaps, however, as an application to sores, platinised asbestos, either alone or in combination with platinised charcoal, might be found more manageable. In those diseases also where the internal use of charcoal has been found beneficial, I should think that platinised charcoal may be advantageously substituted. In Bunsen's carbon battery also, the employment of platinised charcoal may, I think, be advantageously tried.

It is clear that the amount of platinum in the charcoal may be varied almost at pleasure, according to the strength of the platinum solution employed in its preparation, and the purposes to which the charcoal is intended to be applied. Almost any form, and even very considerable dimensions, may be given to the platinised charcoal,—circumstances which greatly extend the range of its applications.

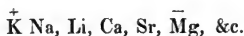
IX.—*On the Preparation of Strontium and Magnesium.*

By A. MATTHIESSEN, PH.D.

IN my paper on the preparation of calcium, I confirmed Bunsen's statement concerning the action of the density of the current employed in the electrolytic decomposition of metallic salts. Since then, in pursuing the research further in the Heidelberg Laboratory, I have found that the same conditions are necessary for the preparation of metallic strontium.

The best method, by which pieces weighing half a gramme are sometimes obtained, is as follows:—A small crucible, with a porous cell, is filled with the anhydrous chloride of strontium mixed with some chloride of ammonium, so that the level of the fused chloride in the cell is much higher than in the crucible. The negative pole placed in the cell consists of a very fine iron wire, wound round a thicker one, and then covered with a piece of tobacco-pipe stem, so that only about the one-sixteenth part of an inch appears below; the positive is an iron cylinder placed in the crucible round the cell. It is easy to regulate the heat during the experiment, so that a crust may form in the cell; the metal will then collect under this crust without coming in contact with the sides. I have found this method very advantageous also for the preparation of calcium.

Strontium resembles calcium in colour, being only a shade darker. It oxidises much more quickly than that metal. The specific gravity of the metal obtained from pure chloride of strontium gave in two experiments 2.5041 and 2.5796, the mean of which is 2.5418. Its atomic volume is 216, being $1\frac{1}{2}$ greater than that of calcium. The specific gravity of calcium from pure chloride of calcium gave in three experiments 1.5843, 1.5656, and 1.5835, the mean of which is 1.5778. The atomic volume is 158. The place of strontium in the electrical series, water being used as the exciting liquid, is not the same as has hitherto been supposed, but is as follows:—



Strontium burns like calcium, and also acts similarly to it when heated in chlorine, oxygen, bromine, or iodine, or on boiling sulphur, or when thrown into water or acids.

I next proceed to describe a method of preparing magnesium without the necessity of making the anhydrous chloride, out of which

Bunsen reduces it.* Instead of the anhydrous chloride, the preparation of which is so very difficult, it is simpler to use a mixture of the chlorides of potassium and magnesium in nearly equal proportions: viz. three equivalents of chloride of potassium to four of chloride of magnesium. The solution of the chloride of magnesium can be evaporated almost to dryness and analysed, to find the amount of anhydrous salt present. After having mixed the two salts in the proper proportions with some chloride of ammonium, the mixture may be fused and electrolysed by Bunsen's method, the pockets not being required, as the metal is specifically heavier than the fused mixture. A very simple and convenient way of reducing the metal, especially for the lecture table, is in a common clay tobacco-pipe, over a Berzelius' spirit-lamp, the negative pole being an iron wire put up the pipe-stem, and the positive being a piece of gas-coke just touching the surface of the fused chlorides.

* Ann. Ch. Pharm. lxxxii. 137.

REPORT OF THE COUNCIL,

MARCH 30, 1855.

THE Council have the satisfaction to announce that there is a steady increase in the numbers of the Chemical Society. At the last Anniversary meeting the number of Fellows was—

Resident and Non-resident	247
Deduct Deaths	3
	<hr/>
	244
Add Elected since	17
	<hr/>
Present number of Fellows	261

The Fellows who have died in the last year are Mr. Richard Prosser, of Birmingham; Mr. John Thomas Cooper; and Mr. Charles Blachford Mansfield.

Richard Prosser was an engineer of high original faculties and great attainments. He was the inventor of many mechanical improvements, and among other inventions, of the process of forming pottery from dry clay-dust by the application of powerful pressure, a process which gave rise to the manufacture of those coloured mosaic tiles manufactured by Minton, which have attained so great a celebrity. To the exertions of Mr. Prosser, the late reform in the Patent Law was mainly owing. At the time of his death he was sedulously pursuing a work of importance to the Ordnance Board—an appendix to the volume now issuing from the office of Mr. Woodcroft, containing an account of all the patented inventions on the subject of Gunnery from the earliest periods. He died at the age of 50.

John Thomas Cooper was born at Greenwich, June 29, 1790. In early life he studied for the medical profession; but Chemistry was his favourite science, and we find him at 20 years of age delivering popular lectures on that subject in Mount Street, Lambeth. He was

subsequently appointed Lecturer on Chemistry at the Russell Institution, and he was afterwards teacher of the same science at the Aldersgate School of Medicine. At one time, Mr. Cooper was the sole manufacturer of Iodine in this country. He was also a very successful preparer of Potassium and Sodium by the process of Gay Lussac and Thénard, at a time when those metals were sold for ten and twelve guineas the ounce. Among the published results of Mr. Cooper's scientific investigations, we may mention the following :—"On some Combinations of Platinum" (Q. J. S., iii. 119) ; "Analysis of Zinc Ores" (Q. J. S., ix. 19) ; An Examination of the Ancient Ruby Glass (Ann. Phil. vii. 105) ; "Improvements in the Instruments invented by Dr. Wollaston for ascertaining the Refracting Indices of Bodies" (Mem. of Chem. Soc., April 1843) ; "On Catechuic Acid" (Mem. Chem. Soc., Dec. 1843) ; "On the Baroscope, an Instrument for Measuring Heights" (read before the Royal Society, Feb. 1839). He also discovered the Sesquioxide of Carbon, but from delay in his investigation, Mr. Serullas, who also discovered it, had the priority of publication.

In the year 1823, Mr. Cooper received two of the medals of the Society of Arts, for an improved Hydrometer for Saline Solutions, and for an Apparatus for the Analysis of Animal and Vegetable Substances (Journ. Soc. Arts, xli.)

In 1835, he perfected his Oxyhydrogen Microscope, and in conjunction with Mr. Carey, the Optician, produced it for public exhibition. He first employed the Canada balsam for mounting microscopic objects, an invention of great practical utility.

He died Sept. 24, 1854, in his 65th year.

Charles Blachford Mansfield was the son of a clergyman, and was born at Rowner, in Hampshire, in the year 1819. His interest in natural science exhibited itself at a very early age in an intense fondness for natural history, which he always retained. He was educated at Winchester School, and at the University of Cambridge. Subsequently he placed himself as one of the first pupils at the College of Chemistry, under the guidance of Dr. Hofmann. After passing through the ordinary training of the College, he undertook the investigation of the constituent volatile oils of coal-tar, among which he discovered the presence of benzol in considerable quantity. He invented and patented a process for obtaining benzol from coal-tar, and for producing a new light by charging air with its vapour. His researches on this subject appear in Vol. 1 of the Journal of the Chemical Society, and in the volume of the Researches of the Chemical

College, as well as in a pamphlet. The Institute of Civil Engineers awarded to him, for them, the Telford premium.

In the year 1851, he was invited to deliver a course of lectures on the Chemistry of the Metals, at the Royal Institution. The earlier lectures of this course were remarkable for some broad and original generalisations, which were afterwards developed by him in a manuscript work unfortunately left unfinished. During the last seven years of his life he was much occupied with efforts for the amelioration of the condition of the working classes; and his interest in those matters by which science connects itself with social life, may be instanced by some striking letters on the subject of the consumption of smoke contained in late numbers of the "Mechanics' Magazine." On his return from a voyage to tropical South America he devoted much time to the preparation of a work on the constitution of salts, which he completed and placed in a publisher's hands a few days before the accident which put an end to his career.

He had been officially invited to prepare specimens of the products he had extracted from coal tar, for the French Exhibition then about to be opened. In carrying out this purpose, the accidental boiling over of the naphtha from a small still which he had long been using, inflicted injuries on his assistant and set his own clothes on fire. The still itself was in flames, and the only chance of preventing them from extending to the premises, was in removing the whole apparatus. High courage and presence of mind were never wanting to him. He seized the still in his hands, and bore it a sheet of fire to the door. This he was unable to open, and had to escape through the window. It was on the 17th of February, the coldest day of the present year; the ground was covered with snow, and he extinguished the flames with which he was enveloped by rolling himself upon it. The thought of another's danger now flashed on his mind, and he was with difficulty hindered from re-entering the building to rescue his assistant by a person who had come to his aid. He did not escape, however, without complicating his injuries by a violent blow on the head whilst passing through a low wicker door leading into the street. With his hands burnt almost to the bone, his face and head a mass of injuries, his countenance unrecognisable by his dearest friends, besides slighter wounds on the knees and feet, he had to walk a mile, supported by a woman, to a cab, and had himself carried to the Middlesex Hospital, which he reached almost in state of collapse, from the intensity of the cold. There he terminated his life after nine days of lingering agony.

It would be wrong to estimate the man by what he had actually

given to the world. He was cut off at an age, when, with his varied gifts, it would have been easy for him to have completed an ordinary life's work. He had proposed to himself a task so broad that the time failed him to do more than lay the foundation for it. How broad that foundation was, his manuscript works and fragments, which are mostly preparing for publication, may possibly show to the world.

The following are the Fellows and Associates of the Chemical Society elected since March 30, 1854:—

April 3, 1854.—A. Kekulé, Ph.D., Reinhold Hoffmann, Ph.D., Associates.

May 1.—Robt. Railton, Esq., University College; Patrick Duffy, Belfast, Fellows.

May 15.—Hugo W. Müller, Ph.D., 110, Bunhill Row; Charles Greville Williams, Esq., 3, Oxford Court, Cannon Street, Associates.

November 6.—Robert Mortimer Glover, M.D., F.R.S.E., Royal Free Hospital, Gray's Inn Lane; J. Taylor, Esq., 5, Burchfield Terrace, East India Road; Newton Samuelson, Esq., 11, Temple Court, Liverpool; Henry M. Noad, Ph.D., Bark Place, Bayswater; Robert Hunt, Jun., Esq., Government School of Mines; Isaac Newton Loomis, M.D., of Macao, in the State of Georgia, U.S., Fellows.

Messrs. Henry Buff and Richard Tuson, of St. Bartholomew's Hospital, Associates.

November 20.—Mr. James Taylor, Fellow.

December 18.—John S. Abel, Esq., Coquimbo, Chili; Charles Loudon Bloxam, Esq., King's College; Chas. W. Heaton, Esq., 26, Lime Street; Fletcher Norton, Esq., 5, Stanhope Street, Hampstead Road, Fellows.

January 15, 1855.—H. J. Smith, Esq., B.A., Oxford; Mathew Warton Johnson, Esq.; Charles Tookey, Esq., 3, Mitre Street, Claremont Square, Fellows.

February 5.—Messrs. Frederick Stohmann and Frederick Versmann, of University College, Associates.

March 5.—John James Bancroft, Esq., Ruthen, North Wales, Fellow.

The following is the List of Papers read before the Chemical Society from March 30, 1854, to March 30, 1855 :—

April 17, 1854.—Mr. Frederick Field communicated a paper, "On the Composition of a Specimen of Atacamite from the Province of Copiapo, Chili.

May 15.—"On the Occurrence of Ozone and Peroxide of Hydrogen in the Electrolysis of Sulphuric Acid:" by Heinrich Meidinger.

"On the Corrosive Action of Sugar on Iron and other Metals:" by Dr. J. H. Gladstone.

June 19.—"Preliminary Notice on the Action of Ammonia on the Oils and Fats:" by J. H. Rowney, Ph.D.

"On the Action of Iodine on Calomel:" by Dr. R. M. Glover.

"On an unexpected Source of Nitrobenzol:" by Arthur H. Church.

"On the Substitution-compounds obtained by the Action of Nitric Acid on Cotton:" by Edward Ash Hadow.

November 6.—"On the Analysis of a Surface-Soil from the Desert of Atacama:" by Frederick Field.

December 4.—"On the Preparation of Pure Pyroxylic Spirit:" by W. Gould.

December 18.—"On the Produce of Barley Sown in Rocks of various ages:" by Dr. Daubeny.

"Notice of further Experiments as to the Reduction of Metallic Oxides by Peroxide of Barium:" by B. C. Brodie.

January 15, 1855.—"On Thermo-Electric Joints formed with the metals Antimony, Bismuth, and Palladium:" by Richard Adie.

"Investigation of the Vegetable Tallow from a Chinese Plant, the 'Stillingia Sebifera':" by N. S. Maskelyne, M.A., F.G.S.

"On the Absorption of Chlorine in Water:" by H. E. Roscoe, B.A., Ph.D.

February 5.—On a peculiar Efflorescence of Chloride of Potassium:" by Robert Warington.

"On the Preparation of the Metals of the Earths by Electrolysis:" by A. Matthiessen, Ph.D.

February 19.—"On the Thermo-Electrical Currents generated in Elements where Bismuth is used to Form the Joint:" by Richard Adie.

The Society is also indebted to Professor Miller, of King's College, for an able and interesting discourse, "On the Action of Waters on Lead," delivered at the last Meeting of the Society.

The Council have, during the past year, entered into an arrangement with the Royal Society, by reason of which the Fellows of this Society receive the "Proceedings of the Royal Society" free of charge. The Council wish to record their sense of the liberal spirit in which the Royal Society, with a view to the diffusion of scientific intelligence, has met their wishes upon this point.

Several valuable additions have been made to the library of the Society; and the Council beg to call to it the attention of Fellows as a place of deposit for curious works upon Chemistry, and for pamphlets upon chemical subjects, which, collected, are of great interest, but, separately, are often of little or no value to the possessor.

Dr. ROBERT PORRETT (TREASURER) IN ACCOUNT WITH THE CHEMICAL SOCIETY. Cr.

1864. March 27.	To Balance from last Account	£ 105	s. 2	d. 10½	1865. March 28.	By Payment of One Year's Salary to the Librarian	£ 15	s. 0	d. 0
" "	" Subscriptions since received	255	2	0	" "	" Ditto of One Year's Rent to Polytechnic Institution	120	0	0
" "	" Admission Fees from Thirteen New Members	26	0	0	" "	" Ditto to Henry Watts for One Year's Salary as Editor of the Society's Journal	50	0	0
" "	" One Year's Dividend on £300 Three per Cent. Consols, minus Property Tax	8	9	5	" "	" Ditto to H. Baillière for Publishing the Society's Journal	116	8	0
" "	" Rent for the Use of the Rooms by the Ethnological Society to November 1854, and by the Chess Club to Christmas last	30	15	0	" "	" Ditto for Attendance and for Tea and Coffee	23	19	11
" "	" Proceeds of Sale of "Memoirs"	1	14	4	" "	" Ditto to Henry Watts for Translations	5	16	2
					" "	" Ditto for Petty Cash, Postage, Stamps, &c.	5	5	11
					" "	" Ditto to Imperial Gas Company for Gas	7	7	9
					" "	" Ditto to Cavendish Society Subscription, 1855	1	1	0
					" "	" Ditto to Walton and Maberly for Books	3	3	0
					" "	" Ditto to H. Baillière for Books	7	17	0
					" "	" Ditto to Taylor and Francis for Philosophical Magazine	1	15	0
					" "	" Ditto to Charles Whiting for Printing	5	0	0
					" "	" Ditto to the Collector for Poundage	11	14	0
					" "	" Ditto to Royal Society for "Proceedings" sent to the Members of this Society	20	0	0
					" "	" Ditto to Doorkeeper of Polytechnic Institution	1	0	0
					" "	" Balance carried to new Account	31	15	10½
							£ 427	3	7½

R. PORRETT, Treasurer.

London, 28th March, 1855.

Examined and found correct,

J. H. GILBERT, }
G. H. MAKINS, } Auditors.
WM. ODLING.

PROCEEDINGS
AT THE
MEETINGS OF THE CHEMICAL SOCIETY.

April 2, 1855.

Dr. WARREN DE LA RUE, Vice-President, in the Chair.

Specimens of a deposit formed during the preparation of extract of rhubarb were presented by Mr. George Whipple, accompanied by a note, in which the deposit is described as consisting of several undetermined organic substances, together with a considerable proportion of chrysophanic acid. The caustic alkalies dissolve the greater part of the deposit, forming intense crimson solutions, which stain paper of a crimson colour, are changed to yellow by most acids, and yield a crimson lake of great beauty on the addition of alum. Mr. Whipple suggests that this substance may admit of useful application in the arts.

A paper was read :—

“On the Chemical Composition of the Waters of the Metropolis during the Autumn and Winter of 1854 :” by Dr. B. D. Thomson.

April 16, 1855.

Dr. W. A. MILLER, President, in the Chair.

The following donations were announced :—

“Miller’s Elements of Chemistry :” from the President.

“The Literary Gazette :” from the Publishers.

“The Proceedings of the Royal Society :” from the Society.

Mr. Warington delivered a discourse "On the Maintenance of a Permanent Balance between the Animal and Vegetable Kingdoms in a Medium of Fresh or Sea Water."

May 7, 1855.

Dr. W. A. MILLER, President, in the Chair.

David Gamble, Esq., and T. N. Keates, Esq., were admitted Fellows of the Society.

William Gould, Esq., was duly elected a Fellow of the Society.

The following donations were announced:—

"The Journal of the Society of Arts:" from the Society.

"The Journal of the Photographic Society:" from the Society.

"The Literary Gazette:" from the Publishers.

"The Pharmaceutical Journal:" from the Editor.

Dr. Williamson delivered a discourse "On certain Processes recently proposed for the Decomposition of Fats by Water at High Temperatures."

May 21, 1855.

Dr. G. D. LONGSTAFF, Vice-President, in the Chair.

Dr. Noad was admitted a Fellow of the Society.

The following donations were announced:—

"The Literary Gazette:" from the Publishers.

"The Journal of the Society of Arts:" from the Society.

"The Journal of the Franklin Institute:" from the Institute.

Dr. J. H. Gladstone made a short verbal communication on the Influence of Magnetism on Salts in Solution.

Dr. Gilbert delivered a discourse "On the Chemical Statistics of the Animal Body." After which,

A paper was read:—

"On Platinised Charcoal:" by Dr. Stenhouse.

June 4, 1855.

Dr. W. A. MILLER, President, in the Chair.

The following donations were announced:—

“*Tractatus varii*.” by Robert Boyle. 16mo. London, 1676.

“*Opuscules Chimiques*.” by M. de Margraf. Tomes 1 and 2, 12mo. Paris, 1762.

“*Metallurgie*.” by A. M. Grassin. Tomes 1 and 2, 12mo. Paris, 1751.

“*Institute de Chymie*.” by Jacques-Reinhold Spielmann. Tomes 1 and 2, 12mo. Paris, 1770.

“*Rudiments of Chemistry*.” by Samuel Parkes. 12mo. London, 1822.

“*An Essay on Fire*.” by Mark Augustus Pictet. 12mo. London, 1791.

“*Elémens de Chimie Pratique*.” by M. Macquer. Tomes 1 and 2. 12mo. Paris, 1756.

“*Opuscules Chimiques*.” by Pierre Bayen. 8vo. Paris.

“*Philosophical Tracts*.” by Stephen Hales, D.D., F.R.S. 8vo. London, 1739.

“*Essay on the Disinfecting and Medicinal Chlorurets*.” by Thos. Alcock.

“*Chimie du Fer*.” by Le Chevalier Hervé. 8vo. Paris, 1826.

“*Experiments on Bleaching*.” by Francis Horne, M.D. 8vo. Edinburgh, 1756.

“*Chimie Minérale et Analyses de Substances Minérales*.” by M. P. Berthier. 8vo. Paris, 1835.

“*Description of Chemistry*.” by J. F. A. Gottling. 8vo. London, 1791.

“*Course of Chemistry*.” by M. Lemery. 8vo.

“*Pyritologia; or, a History of the Pyrites*.” by J. F. Henckel. 8vo. London, 1757.

“*De l'Analyse des Corps Inorganiques*.” by J. J. Berzelius. 8vo. Paris, 1827.

“*Lectures on Chemistry, read at Guy's Hospital, by William Babington, Alex. Marcet, and W. Allen*.” 8vo. London, 1816.

“*Chemical Lectures, delivered at Guy's Hospital, by W. Allen, John Bostock, and Arthur Aikin*.” 8vo. London, 1822.

“*Elements of the Art of Dyeing*.” by M. Berthollet. 8vo. Edinburgh, 1792.

“*Recherches sur les Bois*.” by M. Eugène Chevandier. 8vo. Paris, 1844.

"Elements of Chymistry:" by M. Macquer. Vols. 1 and 2. 8vo. London, 1758.

"Elements of Chemistry:" by Joseph Francis Jacquin. 8vo. London, 1803.

"Experiments on Animal Heat:" by A. Crawford, M.D. 8vo. London, 1788.

"Experiments in Chemical Philosophy:" by Bryan Higgins, M.D. 8vo. London, 1786.

"A Treatise on the Nature and Properties of Air:" by Tiberius Cavallo, F.R.S. 4to. London, 1781.

"Complete Works on Chemistry:" by J. Rudolph Glauber. Folio, London, 1689.

From Dr. Faraday.

"On the Object of the Salt Condition of the Sea:" by E. J. Chapman. From the Author.

"A Dream of the New Museum." From Dr. Daubeny.

Gustav Magnus and Charles Gerhardt were duly elected Foreign Members of the Society.

Communications were read:—

"On the Preparation of Strontium and Magnesium:" by A. Matthiessen, Ph.D.

"On the Preparation of Lithium:" by Professor Bunsen.

Dr. Longstaff delivered a discourse "On the Explosion at Gateshead in October 1854."

June 18, 1855.

Dr. W. A. MILLER, President, in the Chair.

The following donations were announced:—

"The Journal of the Society of Arts:" from the Society.

"The Literary Gazette:" from the Publishers.

The following papers were read:—

"On the Colour of Chloride of Copper in different states of Hydration:" by J. H. Gladstone, Ph.D., F.R.S.

"On the Proximate Constitution of Chemical Compounds:" by John Joseph Griffin.

NOTICES
OF
PAPERS CONTAINED IN OTHER JOURNALS.
BY HENRY WATTS, B.A., F.C.S.

**Report on the Supply of Spirit of Wine Free from Duty, for Use in the
Arts and Manufactures.**

By Professors Graham, Hofmann, and Redwood.

ADDRESSED TO THE CHAIRMAN OF INLAND REVENUE.

SIR,—We have now the honour to report on the practicability of supplying for commercial purposes, a mixed spirit free from duty, without injury to the revenue,—a subject proposed to us for investigation in your letter of March 25, in the following terms:—

“The attention of Government has for some time been directed to the importance of allowing spirit of wine, free of duty, for use in the arts and manufactures. In order that such a privilege may be granted with safety to the revenue, it is absolutely necessary that means should be devised by which such spirit may first be rendered unfit for human consumption. It is also indispensable—1st. That spirit, after being thus treated, should still be so pure as to be generally available for the purposes to which it is applied in the arts or manufactures. 2nd. That it should not be capable of purification by any simple process of rectification or otherwise, so as to be made palatable by the addition of sweetening or flavouring ingredients.

“It is also highly desirable, that while the mixed spirit should be rendered as offensive as possible to the taste or smell, no decidedly poisonous properties should be communicated.

“Some preliminary inquiries have been made into this subject. Mr. Phillips, one of our surveying-general examiners, has suggested a substance to be mixed in certain proportions with spirit which would interfere very little with its use in the arts, while it would

render it highly unpalatable, although not unwholesome. Dr. Hofmann, as you are aware, has made a number of experiments on spirits mixed in the manner suggested, and obtained very promising results. It is therefore desirable that the subject should be more fully investigated.

"With this view, your attention is directed to the points already indicated, viz. :—

"Whether and by what means, spirit produced in the ordinary mode can be rendered so offensive to the taste or smell, as to make it unfit for human consumption as a beverage, without materially impairing it, either for the manufacture of ethers, or as a solvent of gum-resins, or for any of the purposes in the arts to which it is usually applied.

"Whether, and to what extent, the mixed spirit would resist any process for its purification, or might be so compounded as to make it palatable?

"To what branches of the arts or manufactures it would be safe or desirable to limit the privilege of using such mixed spirit?

"In what manner, under what superintendence, and with what precautions, the spirit should be mixed?

"The Board will also be glad to hear of any suggestions of a practical nature, although not falling within the scope of this commission, which may occur to you in the course of your investigation."

Of the volatile substances which first suggested themselves as proper to be added to alcohol, in order to attain the object proposed, the greater number were soon eliminated as unsuitable, upon a close consideration or actual trial of their properties.

Sulphide of ethyl, and volatile sulphur-compounds analogous to it, communicate their repulsive taste and odour when they are added to alcohol, even in a proportion so minute as 1 to 100,000; and are not removed from the alcohol by rectification or filtration through charcoal. But the sulphide of ethyl was easily separated from the alcohol by means of distillation, after the addition of a little alkali, which is conclusive against its use.

The neutral volatile oils or essences are too easily removed from alcohol by means of dilution with water and distillation. The same objection applies to ordinary ether and to the compound ethers of all classes, the compound ethers being further readily decomposed by distillation with an alkali.

The mixed oils, procured from wood and various other organic substances by the agency of destructive distillation, promised better results. The liquid distilled from caoutchouc, and known as *Caoutchicene*, which is distinguished by a powerful and highly characteristic odour, has the advantage of being composed entirely of neutral hydrocarbons, and is therefore not likely to be acted upon by either

acids or alkalies. These hydrocarbons are also of various degrees of volatility, some of them boiling at a lower and some at a higher point than alcohol itself, which must increase the difficulty of their separation from alcohol by the process of rectification. For experiments in mixing, caoutchicene was prepared by distilling caoutchouc in a glass retort, by a heat gradually rising to redness. The oil was redistilled till its temperature of ebullition rose to 250° centigrade; and the portion which came over below that temperature, amounting to about three-fifths of the original distillate, was alone employed. The caoutchicene so prepared, when mixed with a large proportion of alcohol, evaporates completely in air, and when used as a solvent of resins, leaves on drying an inodorous varnish.

The proportion of caoutchicene which it was found most advantageous to use, was one part to 400 parts of strong alcohol, or 0.25 per cent. of caoutchicene. The spirit used in all the experiments to be described, was of specific gravity 0.828. Such a mixed spirit becomes milky and opaque when diluted with water, but it is remarkable that the caoutchicene exhibits no disposition to separate as an oil and come to the top, even when allowed to stand at rest for many days. Nor was the oil removed from the diluted mixture by agitation with the solvents of caoutchicene, such as benzole and colza oil. Filtration of the diluted mixture through wood charcoal removes the oil in part, but the caoutchicene odour remains seemingly unreduced in intensity. This mixed spirit, when distilled with one-eighth of its weight of potash, still retained the taste and odour of caoutchicene unaltered. When distilled with the same proportion of sulphuric acid, the odour of the mixed spirit was slightly modified, but still remained very decided. The odour of caoutchicene was not removed from the mixed spirit by chlorine.

500 measures of this mixed spirit were diluted with 250 measures of water, which produced turbidity, and distilled by a water-bath. The distillate first collected, amounting to 166 measures, was of specific gravity 0.869; it became turbid by water, had the rank odour of caoutchicene, and was quite unpotable. The second portion of the distillate, amounting to 380 measures, of sp. gr. 0.888, was less offensive, but its odour was still peculiar and disagreeable; the taste of caoutchicene was also sensible and persistent. This distillate became milky with water, and the odour was then more repulsive. The third portion of the distillate, which contained all that remained of the alcohol, amounted to 62 measures of sp. gr. 0.955. It was turbid, from the more fixed oils having distilled over, and possessed the strong taste and odour of caoutchicene.

The second distillate, described above as amounting to 380 measures, of sp. 0.888, was again diluted with half its bulk of water, and redistilled at 212° . The first portion of distillate, amounting to 166 measures, of sp. gr. 0.893, became very turbid with water, and had

a highly decided odour and flavour of caoutchicene, becoming insupportable on the tongue after evaporation of the alcohol. The second portion of the distillate, amounting to 177 measures, of sp. gr. 0.930, was still decidedly marked by the odour of caoutchicene, particularly on dilution, when it became only slightly opalescent. This, which was the most highly purified portion of the distillate, was evidently a spirit which would not be saleable as a beverage.

In another experiment, 500 measures of the mixed spirit containing caoutchicene were first distilled, and 420 measures drawn off. This distillate became turbid with water and had the offensive odour of caoutchicene. Mixed with half its bulk of water, the liquid was redistilled and three fractions collected. The first distillate, amounting to 182 measures, of sp. gr. 0.875, became milky with water, and retained the repulsive odour and taste of caoutchicene in a striking degree of intensity. The second fraction, amounting to 297 measures, of sp. gr. 0.905, became opalescent with water, and had a distinct odour, not very unpleasant, and a taste allied to that of a minthy essential oil. The odour and taste became more highly marked on the addition of water. The third distillate, amounting to 288 measures, of density 0.987, and very aqueous, was offensive in taste and odour.

The second fraction above, which was the most highly purified portion of the liquid, was itself submitted to a new distillation, and brought over in three portions of sp. gr. 0.865, 0.866, and 0.905 respectively. All of them retained a decided taste and odour of caoutchicene.

These experiments show that much of the caoutchicene in the mixed spirit can be separated by repeated distillations, but that a portion adheres to the alcohol with considerable pertinacity. Enough of the caoutchicene appears to be retained in all circumstances to render the alcohol unpalatable as a beverage. On the other hand, the intense and disagreeable odour of spirit so mixed would considerably limit its applications. The odour would not be tolerated in dwelling-houses, nor in shops and warehouses frequented by the public, and the use of the mixed spirit would probably therefore be confined to manufactories.

Our attention has been particularly directed to wood-naphtha (crude pyroxylic or methylic spirit) as the substance to be added to alcohol, by the previous experiments of Mr. G. Phillips and of Dr. Hofmann on the use of that liquid. The application of crude wood-naphtha depends partly upon the empyreumatic oils which it contains, and partly upon the methylic spirit and other substances miscible with water, which constitute the mass of the liquid. It was necessary to examine separately the influence of these two classes of constituents, and first of the empyreumatic oils.

In one series of experiments, a specimen of the oils which had been

separated from wood-spirit in the process of purifying that liquid, was used as the flavouring substance. Two per cent of these oils were dissolved in spirits of wine. This mixed spirit had the strong characteristic odour of crude wood-naphtha, became milky when mixed with water, and was highly unpalatable.

When this mixed spirit, without any addition, was simply distilled by the heat of a water-bath, a small quantity of a dark-brown tarry matter was left behind in the retort, and the proportion of oils in the distilled spirit was greatly reduced. The mixed spirit appeared to be further purified when distilled from anhydrous sulphate of copper, from the protosulphate of iron, or from persulphate of iron. But none of these distillates was potable, and all became turbid with water. The flavour of the same mixed spirit was improved by distillation with one-eighth of its weight of sulphuric acid, but the liquid was still not potable. When the last distillate was again rectified from one-twentieth of its weight of potash, the rank odour of the oils disappeared in a great measure, the odour now retained resembling that of benzole. An attempt was made to remove the odour last described, by diluting the liquid with water, and passing it in the state of vapour over animal charcoal; but the liquid still retained the benzole odour, and was precipitated by water.

The greatest amount of purification was obtained by distillation from potash or lime, the alkali keeping back the creosote; but the mixed spirit still retained the tarry smell of benzole, and was turbid with water. When the mixed spirit so far purified by means of alkali was diluted with water and again distilled, the first half of the new distillate was turbid with water, and even formed a layer of oil on the surface. But the second half of the distillate did not become turbid with water, showing that the benzole product comes off first. This last portion of the alcohol appearing to be restored to a fair degree of purity, it became doubtful whether much dependence could be placed upon the oils of wood-naphtha, for the purpose of mixing, apart from the methylic spirit of the naphtha. An experiment was made with pure benzole itself, mixed in the proportion of one part of benzole to ninety-nine parts of strong alcohol. A considerable portion of benzole was separated from this mixture by dilution with water, the benzole forming an oily film on the surface of the liquid. The liquid, however, continued milky, and retained a strong odour of benzole. When this mixed spirit was diluted with three times its volume of water, and slowly rectified, the first part of the distillate contained much benzole, and became milky with water; while the second half of the distillate did not become turbid with water, and appeared to contain very little benzole. This result affords a very strong presumption that benzole is removable by rectification from alcohol when diluted with water.

Three additional and still more extensive series of experiments were made by means of different varieties of crude wood-naphtha, as this

substance varies considerably in composition. Two of the varieties were procured from Messrs. Turnbull and Co., of Glasgow, one of which was described as "of full strength, but concentrated without destroying the oils;" the other described as taken "at an earlier stage of the process, half strength, and containing more oils than the last." The third material operated upon was a mixture of strong alcohol with five per cent of crude naphtha, prepared at the laboratory of Inland Revenue by Mr. Phillips. But after what has been already said it is unnecessary to enter into the details of these experiments, as the results were similar to the first series. The oils were in a great measure removed from the mixed spirit by simple distillation, or by distillation from potash, and the distilled spirit was chiefly characterised by the taste and comparatively mild odour of methylic spirit or pure wood-spirit. The specimens became as little offensive as alcohol mixed with Turnbull's purified wood-naphtha; and there appeared, therefore, to be no great advantage in using the crude naphtha for mixing in preference to a purer wood-spirit. The question reduced itself to the applicability of pure wood-naphtha for the object in view.

The wood-naphtha hereafter used for mixing with alcohol was of the comparatively pure quality in which it is supplied to the public by Messrs. Turnbull and Co., at the price of 8s. 6d. per gallon. This wood-naphtha was nearly colourless; it mixed with water without becoming turbid in the least degree, and contained no more than a small trace of the oils which give a rank and repulsive odour to many specimens of wood-naphtha. The odour of this purified wood-naphtha was not disagreeable, although well marked and characteristic, being due principally to methylic spirit. The specific gravity of this naphtha was 0.815, and its boiling point 151° F. When thoroughly dehydrated by being distilled three times from half its weight of anhydrous sulphate of copper, one gallon of the liquid gave by fractional distillation the following series of liquids, each amounting to about a pint:—

1st distillate of sp. gr.	0.8067	boiling point	143.6° F.
2nd	"	"	143.3° "
3rd	"	"	146.5° "
4th	"	"	146.5° "
5th	"	"	148° "
6th	"	"	150° "
7th	"	"	151° "
8th	"	"	151° "

Fractions 1 and 2 distilled again together from anhydrous sulphate of copper, retained the low boiling point 143.5° , and had the mean density 0.8057, which is a liquid possessing the lowest boiling point that has been assigned to methylic spirit, but with a somewhat higher

specific gravity, the specific gravity of pure methylic spirit being about 0.800. None of the fractional portions appears to be a single substance. The methylic spirit is probably accompanied in the earlier fractions with acetone of sp. gr. 0.792 and boiling at 132.8° , and acetate of methyl of sp. gr. 0.908 and boiling at 144° ; while some third liquid, of which the nature is unknown, must be present to impart the high boiling point combined with a low specific gravity which distinguishes the later fractions of the distillate.

The presence of five per cent. of this purified wood-naphtha in strong alcohol is easily recognised by its taste and odour, and is more than sufficient to render spirit unsaleable as a beverage, as has been ascertained upon good authority. At the same time the odour of the mixed spirit on evaporating in air is by no means offensive. In solvent power such a mixed spirit is undistinguishable from pure alcohol; and varnishes made by means of it dry readily and acquire no odour or peculiar character from the menstruum. Farther, no practicable means of separating the methylic spirit again and recovering the spirit of wine in a state of purity and suitable as a beverage, appear to exist; while the substance which destroys the potability of the mixed spirit, without impairing its value for many useful purposes, is not itself poisonous or unwholesome,—wood-naphtha, as is well known, having been used to some extent in medicine. The purified wood-naphtha appears indeed to be singularly well adapted for the preparation of a mixed spirit such as the Government desires to supply duty-free to manufacturers. At the same time, a mixed spirit containing ten per cent. of the purified wood-naphtha appears to be preferable to a five per cent. mixture, from the greater facility of recognising the wood-naphtha in the larger proportion, particularly when disguised by the presence of other volatile and odorous substances. A ten per cent. mixture might therefore be issued in the first instance, and the proportion of wood-naphtha be reduced at a later period, if it was found that the change could be made with safety to the revenue. It is accordingly a ten per cent. mixture which we have had tested for the various useful applications of alcohol, because if this mixture was found to meet the requirements of trade, the suitability for the same purpose of any mixture containing a less proportion of wood-naphtha might be easily assumed.

Although wood-naphtha (methylic spirit) and alcohol are of unequal volatility, there being a difference of about thirty degrees between their boiling points, yet no sensible separation of these liquids can be effected by distillation. Both the five and ten per cent. mixtures described were submitted to fractional distillation; but wood-naphtha was found in all the fractions. Even the last eighth portion of the five per cent. mixture, which was not distilled over, but was left behind in the retort, contained abundance of wood-naphtha, the more volatile constituent. In another experiment, to be described in the

sequel, rectification repeated several times failed equally to eliminate the smallest portion of pure methylic spirit from the mixed spirit. The reason of this is, that alcohol which boils at the higher temperature has a denser vapour than methylic spirit, in the proportion of 1·600 to 1·125. The less volume of alcohol vapour which distils over at the boiling point of the mixed spirit is compensated for by the greater weight of that vapour, so that the proportion between the constituents of the mixed spirit appears to be little, if at all, disturbed during the progress of the distillation.

The similarity in chemical constitution of methylic spirit and spirit of wine, both being alcohols, is attended with a remarkable analogy in properties between the two substances, which appears to render their separation by chemical means also a problem of great, if not insuperable, difficulty.

Methylic spirit forms a solid crystalline compound with chloride of calcium,—a property which is taken advantage of in purifying methylic spirit, for scientific purposes, from the other liquids by which it is accompanied in wood-naphtha. Our mixed spirit being first carefully dehydrated by means of sulphate of copper, and reduced to a specific gravity of 0·801, was then mixed with chloride of calcium, in excess, so as to form a thin paste, and distilled by a water-bath heat. Methylic spirit was easily discernible by its odour in the distillate which came over; so that the presence of ordinary alcohol in a large relative proportion appears to prevent the combination of methylic alcohol with chloride of calcium, or to decompose such a compound when formed: for ordinary alcohol, as well as methylic alcohol, has a considerable affinity for the salt in question. When water was subsequently added to the chloride of calcium nearly dry in the retort, and the heat renewed, a liquid came over which possessed a peculiar and disagreeable odour, but appeared to be chiefly composed of ordinary alcohol. This liquid should have been methylic spirit if the experiment of separation had been successful.

The attempt was also made to purify the alcohol of our mixed spirit from its accompanying methylic spirit, by passing the vapour of the two liquids through a long glass tube containing fragments of chloride of calcium, which was kept at a temperature of 212° during the experiment. No absorption, however, of the methylic spirit by the chloride of calcium occurred, but the salt remained unaltered, and the alcohol distilled over and condensed with its original proportion of methylic spirit.

Several experiments were also made on the oxidation of the mixed spirit by means of various proportions of the mixture of bichromate of potash and sulphuric acid, with the view of oxidising and removing the methylic spirit; but without success. The oxidation products were acetic acid and formic acid, accompanied by much aldehyde, and indicated the decomposition of the alcohol as well as of the methylic spirit.

Sulphuric acid is very useful for discovering the presence of common alcohol when mixed with wood-spirit, from the ready production of ordinary sulphuric ether. But for the converse problem of separating a small proportion of wood-spirit from a large proportion of alcohol, sulphuric acid appeared to be wholly inapplicable.

Oxalic acid employed to etherise the mixed spirit seemed at first to promise better results, as the methylic oxalic ether appeared to form more easily than the corresponding ethylic ether. After the cohobation of the dehydrated mixed spirit with oxalic acid for several hours, the liquid which came over on distilling, was alcohol with the proportion of methylic spirit apparently considerably reduced. This alcohol always contained portions of the oxalic ethers, and was liable to become acid from the gradual decomposition of these ethers. The flavour of the methylic spirit, which is at first covered by the rum-like flavour of these ethers, would no doubt come out with time, and prove, as usual, highly disagreeable. No economical process for the purification of the mixed spirit could, we believe, be founded on the action of oxalic acid.

The conclusion from much investigation is, that the removal of wood-naphtha from the ten per cent. mixed spirit, and the restoration of its potability by any simple and economical process, is a most unlikely occurrence. We apprehend no danger whatever to the revenue from this source. The mixture of spirits of wine with ten per cent. of purified wood-naphtha or methylic spirit, which we commend, may be designated *methyiated spirit* for convenience.

The quantity of wood-naphtha which can be commanded appears to be amply sufficient for the new contemplated application of that substance. We are indebted to Mr. John Turnbull for his valuable opinion on this point. "My calculation regarding wood-spirit," that gentleman states, "is a produce of two gallons and a half from a ton of average dry wood, and the production of the United Kingdom amounts annually to 66,000 gallons. This I take as the proceeds of nineteen manufacturers of pyroligneous acid: although you must receive it as a rough guess, still I believe it is not very far from the truth." Much wood-naphtha is also attracted to this country from the continent, owing to the high price which that liquid obtains here as a substitute for alcohol.

We have been favoured with the opinion of Mr. G. Smith, of Whitechapel, one of the most extensive London distillers, on the application of our methyiated spirit as a beverage. He pronounces the methyiated spirit to be quite unfit for the use of the rectifier. He believes also that publicans would never use such a spirit for mixing with their liquors, even in a small proportion. A mixture of gin with one-eighth part of the methyiated spirit was found to be nauseous and unpalatable. In gin mixed with one-sixteenth of methyiated spirit, the flavour of the latter was still very strongly marked.

In gin with one part of methylated spirit in thirty-two, the flavour of the methylic spirit became faint, but it was still perceptible in a mixture of one to sixty-four. The largest proportion of the methylated spirit which it was thought a publican might venture upon adding to his gin was one in thirty-two. Now, the saving to him would be the same fraction of the spirit duty, or proportion of 6s. 2d. per gallon, the duty on spirits of the strength of gin—that is, a profit of 2½d. per gallon. So small a profit would be no compensation for the deterioration in the quality of the gin. The disagreeable odour of the methylic spirit is brought out strongly on mixing the gin with hot water.

The consumption of sweetened and highly-flavoured cordials appears to be greatly inferior to that of gin; a publican in large business, who may retail 1200 gallons of gin per month, not disposing of more than ten or twelve gallons of cordials in the same time. The substances chiefly used in flavouring cordials are caraway, cloves, and aniseed. The methylated spirit could not be used for any of these liquors. Indeed, from their being generally made use of to give an extempore flavour to gin at the option of the customer, more than usual attention must be paid to their own purity of flavour.

The flavour of brandy is too delicate to be tampered with, by the addition of the smallest proportion of methylated spirit. The addition of the latter substance to whisky would require to be guarded against, from the predilection of the consumers of that spirit for a smoky flavour. An experiment has been related to us in which methylic spirit was employed for the sake of its flavour by a Scotch distiller, and mixed with spirits in the minute proportion of one gallon to 1000 gallons. The flavour, although not objected to in the whisky when newly mixed, became rank and disagreeable in the course of two months. The mixing of methylated spirit with that low quality of rum known as Leeward Islands rum, is also to be apprehended, from the great impurity of that spirit, which would render any additional contamination less obvious to the palate. But when the liquid is deliberately examined, the presence of methylic spirit could not escape detection.

Strong alcohol of not more than 0.830 specific gravity should be employed as the basis of the methylated spirit. As the uniformity in quality of the wood-naphtha employed for mixing is important, it should be approved of by the Excise, and also added to the spirit under the inspection of an excise officer. It appears to us that it would be proper to mix the spirit in the distillery, and to declare illegal the possession of the methylated spirit by a rectifier or publican. The retail sale of the methylated spirit would then fall into the hands of oilmen and druggists, who would be supplied directly by the distiller, or through the agency of a wholesale druggist or drysalter.

Although it appears scarcely probable that the methylated spirit will ever find its way into public-houses, it is, nevertheless, desirable to possess means by which, in cases of misapplication, the presence of wood-naphtha could be readily detected and proved in the suspected liquid. The methylated spirit which was operated upon consisted of ninety measures of spirits of wine, of density 0·828, mixed with ten measures of wood-spirit of density 0·815, and had a density of 0·823, as has been already stated, and boiled about 170°. When the methylated spirit was deprived of all water, by distillation from anhydrous sulphate of copper, it boiled at 169°. These temperatures are both very sensibly under 172°·5, the lowest temperature at which absolute alcohol or any mixture of pure alcohol and water can boil. The possession by a sample of spirits of a lower boiling point than the last, would indicate sophistication, particularly if the low boiling point was retained after rectification of the spirits from sulphate of copper, and the fact would suggest the existence of wood-naphtha in the spirits.

The attempt to identify wood-naphtha in spirits by means of chemical tests, must obviously be attended with great difficulties; for the very applicability of wood-naphtha for the purpose of producing an unpotable mixture which can be given to the public without fear of endangering the revenue, excludes the possibility of an easy separation of the two substances; and it may be at once stated that the experiments made with the view of finding an efficient chemical process for the identification of methylic spirit have been unsuccessful, and deserve to be noticed chiefly as affording additional illustrations of the safety of the mixture which is proposed. Fortunately, methylic spirit, even when highly purified,* so as to become deprived of all the tarry and empyreumatic smell which it generally exhibits, possesses so characteristic and persistent an odour and taste, that after a little experience it is not difficult to detect its existence, even when it is highly diluted or masked by the presence of other flavours.

Among the properties of the two alcohols on which possibly a separation might be founded, the different volatility of the two liquids at once suggested itself: absolute boiling alcohol at 173° Fahr., whilst absolute methylic spirit boils at 143° Fahr. In order to test this process, half a gallon of the methylated spirit was submitted to distillation at a comparatively low temperature, and in an apparatus which allowed the less volatile liquid to condense. The first quart which passed over was again distilled, the first part being collected apart, and so on, until at last one-sixteenth of the original bulk of the liquid was obtained as the most volatile portion. This liquid was repeatedly distilled over anhydrous sulphate of copper to remove any water which it might retain; it was found to boil between 168° and 169°, showing

* By conversion into methyl-oxalate, decomposing this substance by ammonia, concentrating the reproduced spirit, and rectifying over anhydrous sulphate of copper, which retains also the ammonia.

that the methylic spirit had been scarcely concentrated by this process. This fact, which at the first glance appears contrary to general experience, has been already explained; it is due, to a certain extent, to the difference of the vapour-densities of the two alcohols; for it is obvious that the smaller amount of alcohol-vapour which forms during distillation, on account of the higher boiling point of alcohol, must be compensated within certain limits by the greater weight this vapour possesses when compared with that of an equal bulk of methylic spirit vapour.

The isolation of the methylic spirit by a series of fractional distillations having proved impossible, the mixture was now boiled for several hours with dehydrated oxalic acid, in order to produce the oxalates of methyl and ethyl. The difference in the boiling point of the two ethers ($363^{\circ} - 321 = 42^{\circ}$) is not much greater than that which is observed with the alcohols from which they are derived. Oxalate of methyl being at the common temperature a solid crystalline substance, while oxalate of ethyl (true oxalic ether) is a liquid, it was hoped that the fractionation of the mixture of the two ethers might be more successful, and that by repeated distillation at last a product might be obtained in which the more volatile methyl-oxalic ether should predominate to such an extent as to crystallise. Experiment, however, showed that the presence even of a minute quantity of the former ether prevents the latter from assuming the solid form.

In studying the action of oxalic acid upon the methylic spirit, it had been observed that if a smaller amount of oxalic acid be used than is necessary for the etherisation of the entire quantity of the mixture, the methylic spirit appeared to be converted into ether with greater facility than the alcohol. Experiments were accordingly made with the view of isolating the methylic spirit by means of this reaction. The mixture was partially etherised by oxalic acid, and then submitted to distillation in order to separate the alcohol which had not been acted upon by the acid. The residuary liquid, consisting chiefly of methyl-oxalic ether, was decomposed by distillation with water. The reproduced spirit certainly contained a larger amount of methylic spirit than the original mixture; nevertheless the quantity of alcohol which it retained was so considerable that the advantages gained by the process did not appear to be in proportion to the amount of time and labour which its practice requires. A further concentration might be obtained by a repetition of the process; but this would render it so tedious and troublesome an operation as to preclude the possibility of using it as a routine test for the purpose of recognising the presence of methylic spirit in a suspected liquid, although the process might be available for identifying and isolating that substance in cases of dispute.

Under the influence of oxidising agents, methylic spirit furnishes, together with other products, a considerable amount of formic acid,

whilst alcohol under these circumstances yields principally acetic acid. Formic and acetic acids, although closely allied in composition and general characters, still offer a greater number of points of difference than the two alcohols which they represent. Formic acid may be readily distinguished from acetic acid by the facility with which the former precipitates the metals from the solutions of the more easily reducible metallic oxides, such as oxide of silver or oxide of mercury, which are not affected by acetic acid. Unfortunately this method of testing became inapplicable, since it was found that alcohol free from methylic spirit, when submitted to the action of oxidising agents, invariably yields, in addition to aldehyde, which can be resinified and removed by potash, a small quantity of formic acid; so that the presence of formic acid among the products of oxidation of a suspected liquid cannot with certainty be regarded as an evidence of the existence of methylic spirit in the original liquid.

It is well known that ordinary alcohol, when heated with an excess of concentrated sulphuric acid, furnishes, in addition to sulphurous acid, a considerable amount of olefiant gas. Methylic spirit, under the same circumstances, gives rise to the formation of a heavy oily liquid, which is insoluble in water, and consists chiefly of the neutral sulphate of methyl. The same liquid was obtained, together with olefiant gas and sulphurous acid, when the methylated spirit was distilled with eight or ten times its weight of concentrated sulphuric acid. But on careful examination, it was found that alcohol alone, when submitted to similar treatment, yields likewise, in addition to olefiant gas, the chief product of the reaction, a small quantity of oily products (heavy oil of wine, &c.); so that the production of an oily substance from a suspected liquid by the action of an excess of sulphuric acid ceases to be an indication of the presence of methylic spirit in such liquid.

The action of sulphuric acid upon the two alcohols produces a very different result if the latter are in excess. Alcohol and methylic spirit under these circumstances exhibit the same deportment, the former yielding ether (common sulphuric ether), while the latter is converted into methyl-ether. It is, however, well known that the etherisation of common alcohol proceeds with far greater ease than that of methylic spirit. Accordingly, the methylated spirit was submitted to the ordinary continuous etherisation-process (ten parts of wood-spirit being successively exposed to one part of sulphuric acid). It was expected that after the evolution of the ether capable of being formed under these circumstances, the methylic spirit would remain behind as sulphomethylic acid. But the residue, neutralised with lime and distilled with water; or with solution of potash, furnished no spirit, but an aqueous liquid in which no methylic spirit could be detected.

When anhydrous baryta is dissolved in dehydrated methylic spirit, a combination is formed, which crystallises in lustrous needles, and

consists of equal equivalents of methylic spirit and baryta. This substance was found to resist the action of water; even when boiled with water, it gave up no methylic spirit. It was possible that alcohol might differ in this respect; but although no crystals were observed, nevertheless a similar compound, with analogous properties, appeared to be formed, a solution of anhydrous baryta in absolute alcohol, when distilled with water, yielding scarcely a trace of alcohol.

Lastly, a few experiments were made with the view of establishing the presence of methylic spirit in alcoholic mixtures by the dark yellowish-brown colour wood-spirit assumes when left for some time in contact with either solid hydrate of potash or soda. But it was found that the brown colour assumed by methylic spirit was only little more intense than that which alcohol shows when similarly treated. Moreover, it seems to be chiefly due to the impurities, the colouration becoming less and less marked the greater the care bestowed upon the purification of the methylic spirit; the pure methylic spirit obtained by decomposing methyl-oxalic ether showing, within a moderate time, no colouration whatever, either when left in contact in the cold, or when boiled with solid hydrate of potash or soda.

The principal uses to which spirit of wine is, or may be, applied, independently of its use as a beverage, appear to be the following:—

As a solvent of resinous substances, which, when thus dissolved, are used in the manufacture of hats, and otherwise as varnishes. As a solvent employed in the manufacture of many chemical preparations, including the alkaloids and other organic products, which are principally used in medicine. For the production of ether, chloroform, sweet spirit of nitre, and fulminating mercury. For burning in spirit-lamps as a source of heat, and for mixing with oil of turpentine or other hydrocarbons for burning in lamps as a source of light. As a solvent and menstruum for administering the active constituents of animal and vegetable substances used in medicine in the form of tincture, spirit, &c. As a solvent of essential oils and other odorous substances used in perfumery.

1. Spirit of wine is largely used for dissolving the resins employed by hatters and varnish-makers.

In the manufacture of *hats*, shellac, dissolved either in spirit of wine or in impure methylic spirit (known as wood-naphtha), is used for giving stiffness and elasticity to the felt or other foundation of the hat, and for causing the adhesion of the nap. When wood-naphtha is used for this purpose, it is necessary to make a selection of those commercial samples which are found to be most suitable. Some varieties of wood-naphtha are imperfect solvents of the resins, and are therefore inapplicable for the purpose; but even among those

samples which freely dissolve the resins, there is much difference in quality, commercial methylic spirit being always a mixed and very variable product, some of the constituents of which exert an injurious effect in the varnishes made with it. Spirit of wine is preferred to wood-naphtha for hat-making, being, in the state in which it is met with in commerce, more uniform in quality, and less contaminated with foreign matters. Hatters state that when the felt has been stiffened with shellac dissolved in spirit of wine, the felt retains its elasticity after it has been dried and hardened, without being much affected by atmospheric changes or exposure to wet, and it does not readily crack or break on being bent. But when the felt has been stiffened with shellac dissolved in naphtha, the hat, while it retains its stiffness, is liable to crack on being bent, and it readily loses its stiffness and elasticity when wetted or exposed to a damp atmosphere. Wood-naphtha is, therefore, used only on account of its low price, the quality of the hats in the manufacture of which it has been used being inferior to that of hats made with solution of shellac in spirit. In those instances in which, from competition in price, the hat-maker is obliged to use wood-naphtha, it is found necessary to use more shellac than would be required if spirit of wine were the solvent, in order to give the required stiffness and elasticity. The weight of the hat is thus increased, sometimes to the extent of several ounces, in order to compensate for the deteriorating effect produced by the naphtha. English hatters generally complain that they have to compete with foreign makers under a disadvantage, in consequence of the high price of spirit in this country.

In the manufacture of *spirit varnishes*, which are applied to other purposes than that of hat-making, both spirit of wine and naphtha are used for dissolving the resins. Among the varnishes of this description are included French polish and lacquer, the consumption of which, as also of other spirit varnishes, is very great. Varnishes made with spirit of wine are considered to be better in quality than those made with naphtha. With regard to French polish, those who are practically engaged in the use of this varnish say that when it is made with wood-naphtha, it is not so easily worked, and does not afford so durable and serviceable a polish as that made with spirit of wine. The disagreeable smell evolved during the evaporation of the wood-naphtha is also objected to, especially when the polish has to be applied to furniture in private houses, or in the warehouses of upholsterers which are visited by customers. In the manufacture of lacquer for brass and other metals, and of other sorts of spirit varnish, there are also equally strong objections to the use of wood-naphtha as a substitute for spirit of wine. Hitherto the French have been considered to excel us in lacquered goods, which may no doubt be ascribed to the superiority of their lacquer, in the manufacture of which they always use spirit of wine for dissolving the resins. English

manufacturers, on the other hand, notwithstanding the inferiority of lacquer and other varnishes made with wood-naphtha, use large quantities of that solvent; in proof of which an extensive varnish-maker informed us that his consumption of wood-naphtha was equal to that of spirit of wine. There is reason to believe that if spirit were supplied to manufacturers duty-free, the use of spirit-varnishes would be greatly extended, and varnished ornamental woods would frequently be substituted for painted deal.

Among the purposes to which spirit varnishes would be more generally applied, if spirit were cheaper, may be mentioned the manufacture of paper-hangings, and especially those in which imitation gold leaf ("leaf metal") is used, which, unless protected with varnish, soon become tarnished by the sulphuretted hydrogen always present in a town atmosphere. Not only for gilt papers, however, but for many others, and especially those used in staircases, would the application of a good spirit varnish be advantageous.

Another application of spirit-varnish would be in the production of waterproof papers, to be used as wrapping-paper for steel goods, for the construction of envelopes for transmission by sea, for the manufacture of military cartridges, &c.

Among the productions of ornamental stationery, there is a class of paper, with embossed patterns, originally called Morocco paper, but which, on account of the variety of the patterns, now appear under the more general designation of varnished papers, which are very extensively used, especially for book-binding, and for cardboard box-making; and in the production of these papers the English manufacturer is at present precluded, by the high price of spirit of wine, from the use of spirit varnish. It is admitted that this manufacture would be greatly improved by the employment of spirit varnish, as the papers, when made, as at present, with oil varnish, are not adapted for exportation, on account of their liability to become heated and to adhere together.

In some of the applications of leather, the employment of spirit varnish would be a great advantage, especially in book-binding. At present its use is restricted by the high price of spirit to the better class of bound books; but its employment not only increases the beauty of the work, but serves to protect the leather; and there can be no doubt that, if spirit were cheaper, its use for this purpose would be greatly extended.

In the application of spirit of wine as a solvent of resinous substances for the purposes already referred to, it is not necessary that the spirit should be pure; but it is important that whatever foreign matter may be mixed with it shall volatilise without producing a very disagreeable odour, and that the resins shall be left, after the drying of the varnishes, unimpaired in quality and free from any offensive smell derived from the solvent.

There is reason to believe that a considerable quantity of illicit spirit is supplied to a certain class of hatters and varnish-makers, to the injury of the revenue and of the honest manufacturer. We are informed that this illicit spirit is sold for about 12s. per gallon, at 60 overproof.

As the employment of spirit for dissolving resinous substances appears to be the most extensive and important of its applications in the arts and manufactures, it was necessary to ascertain whether spirit mixed in the manner proposed in this Report is applicable for such purposes. With the view of determining this point, experiments were made by ourselves, and were also kindly undertaken, at our request, by gentlemen practically engaged in the several departments of manufacture referred to. The results have fully satisfied us that the methylated spirit is suitable for all these applications. We are indebted for much valuable assistance, in reference to this part of our inquiry, to Messrs. J. T. and E. Christy and Co., and Messrs. Cooper, Box, and Co., hatters; to Mr. Rea and Mr. Heywood, varnish-makers, and to Mr. Warren De la Rue.

2. Spirit of wine is employed as a solvent in the manufacture of many chemical preparations, including the alkaloids and other organic products, which are principally used in medicine. In manufacturing the alkaloids derived from the cinchona barks, spirit is used in one part of the process. Indeed, alcohol appears to be the best and most general solvent for this class of substances. It is used in the manufacture of veratrine, and is required for crystallising morphine, although this alkaloid may be prepared from opium without spirit. It has hitherto been the object of English manufacturers to discover processes for the preparation of chemical products without the use of spirit, and such processes are sometimes adopted to the injury of the product. Spirit of wine may be advantageously used in the preparation of some inorganic salts, such as protosulphate of iron, which, when precipitated from its aqueous solution by means of alcohol, is less subject to change from exposure to the air than it is when crystallised in the usual way. The resinous constituents of jalap and scammony which are used in medicine, are separated from the drugs by means of spirit of wine, and the use of this solvent might no doubt be greatly extended for similar purposes with advantage. In some cases the manufacture of chemical products has been lost to English manufacturers in consequence of the high price of alcohol or of ether which is made from alcohol. Thus, pure tannin, the preparation of which involves the loss of a large quantity of ether, is imported from abroad at a price at which it cannot be produced at home. Among this class of productions, involving the use of spirit of wine as a solvent, may be mentioned transparent soap, a pure and elegant preparation for the toilet, which is much used in those countries in which alcohol is cheap, but which, from the

high price of the solvent, is but rarely made and little used in this country.

For all the purposes here referred to, the methylated spirit appears to be applicable. In addition to our own experiments, we have been favoured with a statement of results obtained by Mr. T. N. R. Morson, in the preparation of chemical products, and by Mr. Pears in the manufacture of transparent soap.

3. Spirit of wine is used as an ingredient for the production of ether, chloroform, sweet spirit of nitre, and fulminating mercury. These are important articles of manufacture, the first three articles being valuable medicinal agents, and the last-named being used for making percussion caps for fire-arms. Ether and chloroform are also made use of on account of their solvent power, especially the former. Sweet spirit of nitre is used exclusively in medicine, but being a popular remedy, the quantity used is very considerable. We may state with reference to this article, that it is made by distilling a mixture of spirit of wine and nitric acid, and that when properly prepared it consists of a solution of a small quantity of nitrous ether in spirit of wine. The proportion of nitrous ether present is extremely variable, and in some commercial samples is so small as merely to impart a slight flavour to the spirit, which flavour, moreover, is by no means disagreeable. From information derived from those practically acquainted with the commerce of this article, it may be inferred that a large proportion of the sweet spirit of nitre now used is made from illicit spirit, the price at which the wholesale dealer can purchase sweet spirit of nitre being less than that at which it can be produced with spirit on which the duty has been paid. It is scarcely to be expected that spirit which has been rendered permanently unpotable can be used for making sweet spirit of nitre, as the peculiar and unobjectionable flavour of that compound is the popular test of its good quality. When made with the methylated spirit, the compound acquires a disagreeable flavour, which is more especially developed on diluting it with water; and it is impossible to recover the alcohol again in a pure state from such sweet spirit of nitre. On the other hand, the separation of pure alcohol from good potable sweet spirit of nitre, such as the public are accustomed to use and require, is attended with no difficulty. It appears improbable, therefore, that any regulations could be devised for the preparation of sweet spirit of nitre from duty-free spirit, which could be adopted with safety to the revenue.

Ether and chloroform may be made with the methylated spirit, and when the products have been purified in the usual way they do not appear upon a superficial examination to differ from those made with pure spirit. Upon allowing them slowly to evaporate, however, a peculiar and disagreeable odour becomes perceptible towards the end of the evaporation. This impurity would probably preclude their

application for most medicinal purposes, for which they are required to be pure, or at least to be free from any foreign flavour either in taste or smell. When used as solvents, the same degree of purity is not generally essential, and we believe that ether and chloroform produced from the mixed spirit are perfectly applicable for most manufacturing purposes.

Fulminating mercury is produced from mercury, nitric acid, and alcohol, and in consequence of the large quantity of alcohol consumed in the process, the price of the product is greatly influenced by the cost of this ingredient, so that the English manufacturer has found it difficult to compete with those who can command cheap spirit. We are informed that most of the fulminating mercury now used in this country is either made from illicit spirit, or is brought from the Channel Islands, where the low price of spirit offers an advantage to the manufacturer. The methylated spirit is applicable for this manufacture.

We have been aided in this part of our inquiry by the information kindly afforded to us by Mr. Alfred White, Mr. Charles Davy, and Mr. F. Joyce.

4. A considerable quantity of spirit of wine is sold by retail dealers, chiefly chemists and druggists, for burning in lamps as a source of heat, including its application for singeing horses. It is also mixed with oil of turpentine or other hydrocarbons for burning in lamps as a source of light. The methylated spirit is quite suitable for such applications.

5. Spirit of wine is used as a solvent and menstruum for administering the active constituents of animal and vegetable substances used in medicine in the form of tincture, spirit, &c. These preparations being intended for the treatment of disease, and their efficacy frequently depending upon the association of substances which from long experience have been found to contribute to the required result, the unauthorised introduction into their composition of a new substance, and especially one of so marked a character as methylic spirit, cannot in any way be sanctioned. There is a large number of pharmaceutical preparations of the sort here referred to, most of which are made according to formulæ given in the Pharmacopœias, a strict compliance with which is enjoined upon those who compound them. We cannot recommend the substitution of any mixture for the pure spirit directed to be used in making these preparations.

6. Spirit of wine is employed as a solvent of essential oils and other odorous substances used in perfumery, and it is scarcely necessary to say that the addition of anything to the spirit imparting to it an unpleasant odour must render it unfit for purposes of that description. The methylated spirit, therefore, cannot be used for the preparation of perfumes.

7. The employment of spirit of wine in the manufacture of acetic acid by the German process of oxidation has been suggested as a possible result of the entire removal of the duty on pure spirit; but this application could not obviously be made of a mixed spirit, such as has been contemplated in this inquiry.

8. The methylated spirit would serve for the preservation of objects of natural history, and also for the purposes generally to which alcohol is applied in chemical research. It would remove an impediment to the prosecution of science in this country, created by the high price of alcohol, which has long been complained of.

To recapitulate briefly the results of this inquiry—

It has appeared that means exist by which spirit of wine produced in the usual way may be rendered unfit for human consumption as a beverage, without materially impairing it for the greater number of the more valuable purposes in the arts to which spirit is usually applied. To spirit of wine of not less strength than corresponds to density 0.830, it is proposed to make an addition of 10 per cent. of purified wood-naphtha, otherwise known as wood-spirit, pyroxylic spirit, and methylic spirit, and to issue this mixed spirit for consumption, duty free, under the name of "Methylated Spirit." It has been shown that methylated spirit resists any process for its purification, the removal of the substance added to the spirit of wine being not only difficult, but to all appearance impossible; and further, that no danger is to be apprehended of the methylated spirit being ever compounded so as to make it palatable. The privilege of using such mixed spirit should be open to all branches of the arts and manufactures without restriction; but it may be expedient to prevent the sale of methylated spirit in licensed public-houses, or the preparation and sale of it by the licensed rectifiers of spirits. The wood-naphtha employed in mixing should be supplied by the Inland Revenue, in order to ensure uniformity in its quality, and that substance be mixed with the spirit at the distillery, under Government inspection. The permission to use pure spirit of wine for any purpose of manufacture, under a bond of security, or in presence of a revenue officer, may reasonably be withheld till the methylated spirit now proposed has had a fair trial. It may be found safe to reduce eventually the proportion of the mixing ingredient to 5 per cent., or even a smaller proportion, although it is recommended to begin with the larger proportion of 10 per cent. The present supply of wood-naphtha is amply sufficient for the application contemplated of that substance, for mixing with the spirits used in the arts and manufactures of the country.

The command of alcohol at a low price is sure to suggest a multitude of improved processes and of novel applications, which can be scarcely anticipated at the present moment. It will be felt far beyond the

limited range of the trades now more immediately concerned in the consumption of spirits; like the repeal of the duty on salt, it will at once most vitally affect the chemical arts, and cannot fail ultimately to exert a beneficial influence upon many branches of industry. The same measure also practically removes one of the last anomalies in the duties imposed for revenue; alcohol having, as a raw material of manufacture, a claim to exemption from duty according to sound principles of taxation.

We have the honour to remain,

Sir,

Your very obedient Servants,

THOMAS GRAHAM.
A. W. HOFMANN.
THEOPHILUS REDWOOD.

London, July 24, 1854.

JOHN WOOD, Esq.,
Chairman of the Board of Inland Revenue.

Inland Revenue, 2d November, 1854.

GENTLEMEN,—

As I am informed that it is your intention to add some remarks to your report on the supply of spirit of wine duty-free for use in the arts and manufactures, I take the opportunity of requesting your attention to the passage in page 8 of the Report, in which you state, in effect, that as the oils in crude naphtha are removable from the mixed spirit by a process not very difficult, the question is reduced to the applicability of pure wood-naphtha for the object in view.

I am not entirely convinced that the question is thus narrowed. We have two objects: first, to prevent the recovery of spirit of wine from the mixture in such a state of purity as to render it potable; and, second, to render the mixed spirit so offensive as to prevent any temptation to its use among the workpeople, who will necessarily have access to it in the manufacturing processes in which it will be employed.

Now, it is obvious that the use of crude naphtha produces a more offensive mixture than that of the pure naphtha; and that it would probably be so offensive as to preclude its consumption by workpeople; and this would be an important point gained.

It is also obvious that any attempt to render it potable (as an article of commerce) would be more troublesome and expensive.

The question, then, remains, whether the crude mixture would be generally available in arts and manufactures.

This is a subject of great practical importance, and I shall be much obliged by your attention to it, and by the communication of the result of your inquiries.

I am, &c.,

(Signed)

JOHN WOOD.

Thomas Graham, Esq., F.R.S.
A. W. Hofmann, Esq., F.R.S.
Theophilus Redwood, Esq.

London, 8th January, 1855.

SIR,—

The observations which we desired to add to our "Report on the Supply of Spirit of Wine, free from Duty, for use in the Arts and Manufactures," have reference to the mode in which the public is to be supplied with the spirit. On a review of the subject, and after further inquiries among manufacturers and others, we doubt whether it would prudent to permit, at first, the retail sale of the methylated spirit. It has been represented to us that the unrestricted sale of the spirit would cause it to get into the hands of individuals of perverted tastes, who, in extreme cases, may use it for producing intoxication. Although we are satisfied that such a misapplication of the methylated spirit could only occur in some isolated instances among persons of confirmed habits of intemperance, yet it may be feared that even such cases would cause a public outcry against the measure before it had received a fair trial. We would, therefore, recommend that the methylated spirit should be issued, by agents duly authorised by the Board of Inland Revenue, to none but manufacturers, who should themselves consume it, and that application should always be made for it according to a recognised form, in which, besides the quantity wanted, the applicant should state the use to which it is to be applied, and undertake that it should be applied for that purpose only. The manufacturer might be permitted to retail varnishes and other products containing the methylated spirit, but not the methylated spirit itself in an unaltered state.

In thus suggesting a restriction upon the sale of the methylated spirit, we must, however, express our belief that this limitation may eventually be removed with safety when the measure has been fairly and fully introduced.

Our attention having been directed, by your letter of the 2d November 1854, to that part of our Report in which we recommend the use of purified wood-naphtha, rather than crude naphtha, for preparing the methylated spirit, we have instituted new inquiries on this part of the subject.

We have, in the first place, to state, that the distinction of crude and purified wood-naphtha is not generally recognised in commerce. The term "crude wood-naphtha," when used, is understood to designate a very impure sort of naphtha, not in the state in which that substance is first produced, but in a partially, although very imperfectly, purified state. This product, which is of a brown colour, and contains tarry matter and oils which are not easily volatilized, after being further purified, constitutes the wood-naphtha generally met with in commerce, and which we have referred to as purified wood-naphtha. The terms "crude" and "purified," as thus applied, have not any definite signification; they are used to indicate an undefinable difference of purity, the principal feature of which consists in the presence of more difficultly volatilized matter in the less pure than in the more highly purified article.

We have further to state, that the purification of crude naphtha, to the extent to which this is effected for commercial purposes, is not attended with any difficulty. Methylated spirit prepared with crude naphtha may also be rendered as free from taste and smell as that made with purified wood-naphtha, by simple and inexpensive means.

We have had a methylated spirit prepared (No. 1 of the specimens sent herewith), containing 10 per cent. of the crudest wood-naphtha we could procure, and which was quite unsaleable. Now, by a simple distillation from 10 per cent. of potash, this (as seen in No. 2) is highly purified, so as to be quite equal, if not superior, to the methylated spirit made with Turnbull's purified wood-naphtha, as recommended in the Report. The cost of applying this purification of methylated spirit would be less than 1s. a gallon.

We believe that if very impure wood-naphtha be used for making the methylated spirit, the spirit so prepared will not fulfil the requirements of any class of manufacturers referred to in our Report, unless the purification of the spirit before its use be permitted, and such; we presume, would not be deemed advisable; if this purification was forbidden, the honest manufacturer would obey the law, and work to a great disadvantage as compared with his less scrupulous competitors, who would resort to illicit purification. This of itself would be a great evil, and one, we fear, quite beyond the powers of the Excise to prevent. We admit that the methylated spirit made with crude naphtha would be more unpalatable than that made with purified wood-naphtha, and that the latter would be more likely than the former to be drunk by the workmen employed in manufactories where such spirit was used; but, as already stated, we can only conceive it possible that such use would be made of methylated spirit by individuals of perverted taste, and confirmed habits of intemperance; and in such instances we doubt if even the use of crude wood-naphtha would be sufficient entirely to prevent the evil.

The conclusions we have come to as the result of our investigations

on this subject are, that methylated spirit made with a very impure wood-naphtha could not be advantageously used as a solvent for resins by hatters and varnish-makers, as the less volatile parts of the naphtha would be retained by the resins after the spirit had evaporated, and the quality of the resins would be thus impaired, and that such methylated spirit would be almost wholly inapplicable for chemical and pharmaceutical purposes, and for the preservation of objects of natural history. The benefits anticipated from the proposed measure would thus be greatly limited, without, as we believe, any adequate advantage resulting, either in increased security to the revenue, or otherwise.

It is purified wood-naphtha, and not the impurity which crude naphtha contains, that presents the great and insuperable difficulty we have indicated to its separation from spirit of wine with which it has been mixed; in fact, the more highly purified the naphtha is with which the spirit is mixed, the more difficult it will be to effect an alteration of this mixture in the way contemplated by any chemical process; and in proportion as this condition is fulfilled, the mixed spirit will be more valuable for use in the arts and manufactures as a substitute for spirit of wine: on the other hand, the impurity which constitutes the difference between crude and purified wood-naphtha presents little or no difficulty in the way of its separation, whilst for all purposes referred to it renders the mixed spirit contained in it less applicable, and for some of those purposes it entirely precludes its application.

We are, therefore, unable to recommend any alteration in the mode of preparing the methylated spirit suggested in our Report.

THOMAS GRAHAM.
A. W. HOFMANN.
T. REDWOOD.

To John Wood, Esq.,
Chairman of the Board of Inland Revenue.

On the Preparation of Lithium.*

(Copy of a Letter addressed to Professor Liebig by Professor Bunsen.)

DR. MATTHIESSEN is still engaged with the preparation of the metals of the alkaline earths. Out of the chloride of lithium which you had the kindness to send me, I have with him reduced the metal. This, which is more easily obtained than the other metals belonging to the same group, can be prepared at the lecture-table with the greatest success. The method by which we prepare it is the following:—Pure chloride of lithium is fused over a Berzelius's spirit lamp in a small thick porcelain crucible, and is decomposed by a zinc coke battery consisting of four to six cells. The positive pole is a

* Ann. Ch. Pharm. xciv. 107.

small splinter of gas coke (the hard carbon deposit in the gas retorts), and the negative an iron wire about the thickness of a knitting needle. After a few seconds, a small silver-white regulus is formed under the fused chloride round the iron wire and adhering to it, which after two or three minutes attains the size of a small pea: to obtain the metal, the wire pole and regulus are lifted out of the fused mass by a small flat spoon-shaped iron spatula. The wire can then be withdrawn from the still melted metal, which is protected from ignition by the chloride of lithium with which it is coated. The metal may now be easily taken off the spatula with a pen-knife, after having been cooled under rock-oil. As this operation can be repeated every three minutes, an ounce of chloride of lithium may be reduced in a very short time.

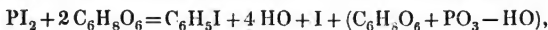
Lithium on a fresh cut surface has the colour of silver, but tarnishes after having been exposed for a few seconds to the air, and becomes slightly yellow. The melting point is 180°C . A piece of it at that temperature, if pressed between two glass surfaces, exhibits the colour and brightness of polished silver. Lithium is harder than potassium or sodium, but softer than lead, and therefore can be pressed out like that metal to wire. The specimen I enclose, about a foot in length, weighs only nine milligrammes. It tears much more easily than a lead wire of the same dimensions. By pressure, lithium can be welded at ordinary temperatures: it swims on rock-oil, and is the lightest of all solid bodies. Its specific gravity is 0.5936, being the mean of two experiments. The first, in which the chloride of lithium used was precipitated twice with carbonate of ammonia, gave as result 0.5983; in the second, the chloride was three times precipitated, and gave 0.5891. If the atomic weight of lithium be taken at 81.7, its atomic volume is 13.7, being nearly the same as that of calcium.

Lithium is much less oxidisable than potassium or sodium. All these metals mark paper. Potassium marks it whitish-grey, and disappears first; then sodium, which gives a bluish-grey tint; and last of all, lithium, which marks it lead-grey. Lithium ignites at a temperature much higher than its fusing point; it burns tranquilly, with an intense white light. It burns when heated in chlorine, oxygen, bromine, iodine, or dry carbonic acid, and on boiling sulphur with uncommon brilliancy. When thrown on water, it oxidises, but does not fuse as sodium does. Fuming and common nitric acid act on it so violently that it fuses, and often ignites. Concentrated sulphuric acid attacks it slowly, but diluted sulphuric and hydrochloric acids quickly. Silicic acid, glass, and porcelain, are attacked by lithium at a temperature even below 200°C .

On the Action of Iodide of Phosphorus upon Glycerine.*

By MM. Berthelot and De Luca.

WHEN 1 part of crystallised biniodide of phosphorus and 1 part of syrupy glycerine are mixed together, a very energetic action soon takes place; *propylene* C_3H_6 , is evolved in the form of gas; water and liquid *iodopropylene* C_3H_5I distil over; and there remains in the retort a solid mass composed of iodine, undecomposed glycerine, a small quantity of an organic compound containing iodine, together with oxygen-acids of phosphorus and a trace of red phosphorus. With 1 eq. iodide of phosphorus and variable quantities of glycerine, the products are 1 eq. iodopropylene and 4 eq. water. To obtain 1 eq. of propylene-gas, it is necessary to use from 9 to 18 eq. of iodide of phosphorus; hence the formation of propylene is but of secondary importance as compared with that of iodopropylene. The residue in the retort is of variable composition. When 100 parts of iodide of phosphorus are made to act on 100 parts or more of glycerine, the products just mentioned are formed, and the residue consists mainly of glycerine; but when only 64 parts, or a smaller quantity of glycerine is used to 100 iodide of phosphorus, the residue in the retort consists of a black, non-volatile, insoluble mass; the point at which this change in the reaction takes place corresponds nearly to the proportion of 2 eq. glycerine to 1 eq. iodide of phosphorus. Half the iodine of the iodide of phosphorus used contributes rather to the formation of the iodopropylene, but remains in the residue under various forms, chiefly, however, in the free state. The principal reaction which iodide of phosphorus exerts upon glycerine appears to be that which is represented by the following equation:—



the portion within the brackets representing the oxygen-acids of phosphorus, mixed and combined with the excess of glycerine. The formation of iodopropylene is due to a reducing action exerted by the iodide of phosphorus on the oxygen of the glycerine.

Iodopropylene, C_3H_5I , constitutes the greater part of the distillate obtained in this decomposition. The latter is rectified, and the liquid which passes over at 101° received in a separate vessel. Iodopropylene thus obtained is a colourless liquid, having an ethereal and afterwards alliaceous odour, insoluble in water, soluble in alcohol and ether, and of specific gravity 1.789 at 16° .

* Compt. rend. xxxix. 745; Ann. Ch. Phys. [3] xliiii. 257.

	Found.	Calculated.
Carbon	21·5	21·4
Hydrogen	3·2	3·0
Iodine	75·7	75·6
	<hr/> 100·4	<hr/> 100·0

Under the influence of air and light, it quickly turns brown, and then emits extremely irritating vapours.

By the action of aqueous ammonia at 100°, continued for forty hours, iodopropylene is completely decomposed; and if the resulting mass be distilled with potash, a very volatile base is obtained, which is insoluble in water, and smells of ammonia and also like sea-fish. This base forms a hydrochlorate, which is soluble in anhydrous alcohol and deliquescent; and the hydrochlorate forms with bichloride of platinum a double salt, which crystallises in yellow needles, dissolves in boiling water, and has the composition of chloroplatinate of propylamine, C_3H_5N , HCl , $PtCl_2$.

	Found.				Calculated.
Carbon . .	13·2	13·0	13·1	—	13·6
Hydrogen . .	3·9	3·8	3·8	—	3·8
Platinum . .	—	37·5	37·6	37·9	37·3

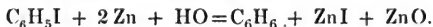
This double salt, when gently heated with potash, is suddenly decomposed, with formation of an inflammable gas, which smells like ammonia and sea-fish, and dissolves in water,—and of a liquid which has a similar odour, a strong alkaline reaction, and on addition of lumps of solid caustic potash, or on being heated to 50° or 60°, boils and gives off an inflammable ammoniacal vapour.

It appears, then, that the action of aqueous ammonia at 100° produces hydriodate of propylene: but this is not the only product formed. If the liquid containing potash, from which the propylamine has been driven out by boiling, is mixed with a slight excess of hydrochloric acid and evaporated in the water-bath, long violet-black needles are produced, which fuse when heated, and are decomposed with evolution of iodine, leaving a residue of charcoal; they are insoluble in water, somewhat soluble in a hot solution of iodide of potassium, scarcely or not at all in sulphide of carbon, and but sparingly in anhydrous alcohol and in ether. The composition of the dark needles recrystallised from ether was not ascertained with certainty, but two analyses gave the following results:—

Carbon	26·0	23·0
Hydrogen	4·1	2·4
Nitrogen	1·5	0·3
Iodine	61·6	69·8

Fuming nitric acid instantly decomposes iodopropylene, with separation of iodine. Sulphuric acid does not act on iodopropylene in the cold; but on the application of heat it carbonises the latter, and a small quantity of propylene gas is evolved.

By the action of hydrogen-gas in the nascent state, iodopropylene is converted into propylene. When iodopropylene is added to a small quantity of zinc and dilute sulphuric acid, and the mixture gently heated, the iodopropylene is decomposed, and a gas is evolved, the fourth part of which consists of propylene:



When a small quantity of iodopropylene and dilute sulphuric, or, better, strong hydrochloric acid, are introduced into a test-tube standing over mercury, the latter is attacked, and pure propylene gas is evolved.

Propylene gas may be obtained in the pure state by collecting either the gas evolved in the action of iodide of phosphorus upon glycerine, or that which is produced by the decomposition of iodopropylene with mercury and hydrochloric acid, as just described. The gas obtained by the former method contains a certain quantity of phosphuretted hydrogen; the second method yields propylene-gas mixed with a little hydrochloric acid gas, and a small quantity of the vapour of a chloruretted or ioduretted body, which latter may be completely condensed by passing the gas through a tube cooled to -40° . Large quantities of propylene gas may be readily obtained by mixing in a tubulated retort 50 grms. of biniodide of phosphorus PI_2 (prepared by dissolving phosphorus, together with eight times its weight of iodine, in sulphide of carbon, and evaporating the solution in a stream of carbonic acid gas) with 50 grms. of syrupy glycerine, and inducing the action by a gentle heat; 30 grms. of iodopropylene then collect in the receiver. This product is introduced into a small flask with 150 grms. of mercury and 50 to 60 grms. of fuming hydrochloric acid, and gently heated; propylene-gas is then immediately evolved, and may be collected to the amount of about 3 litres. The eudiometric analysis of propylene-gas gave numbers corresponding with the formula C_6H_6 ; the specific gravity was found to be $= 1.498$, while the density calculated from the formula for a condensation to 4 volumes is 1.478.

Pure propylene-gas has a peculiar and somewhat phosphorous odour, like that of purified olefiant-gas; its taste is sweetish and suffocating. It is not condensed by cooling down to -40° ; but when it was introduced into the narrow neck of a glass tube, the body of which was filled with mercury, its condensation was effected by the expansion of the mercury in heating, at a pressure which appeared to be intermediate between those which are required for the condensation of ammonia and of carbonic acid respectively. Water

absorbs from one-tenth to one-sixth, absolute alcohol twelve to thirteen times, and glacial acetic acid five times its volume of propylene-gas. Fuming or concentrated sulphuric acid absorbs propylene-gas readily: bromine absorbs and combines with it.

When a small quantity of iodine is introduced into a glass globe filled with propylene-gas, and the globe exposed to sunshine for an hour, or heated for some time to 50° or 60° , a liquid product is formed, which may be purified by agitation with potash. This liquid has a density of 2.490 at 18.5° ; when recently prepared, it is colourless, and has an ethereal odour, but becomes coloured by the action of the air, and more especially of light, and then exerts an extremely irritating action on the eyes. It is the biniodide of propylene, $C_6H_6I_2$ —

Carbon	12.4	12.2
Hydrogen	1.9	2.0
Iodine	85.8	85.8
	<hr/>	<hr/>
	100.1	100.0

This liquid does not solidify at -10° . Heated with potash and alcohol, it reproduces propylene-gas, together with a few drops of a volatile compound different from iodopropylene, and probably containing oxygen.

On the Formation of Alcohol from Olefiant Gas.

By M. Berthelot.

A LARGE glass globe of 31 or 32 litres capacity was exhausted of air and filled with olefiant gas; 900 grammes of pure and boiled sulphuric acid poured into it in several separate portions; then a few kilogrammes of mercury; and the whole submitted to violent and continued agitation: the gas was then gradually absorbed. After 53,000 agitations, the absorption became too slow, and the operation was discontinued; the quantity thus absorbed amounted to 30 litres. The sulphuric acid was then mixed with five or six times its bulk of distilled water, and after repeated distillation and subsequent separations with carbonate of potash, 52 grammes of hydrated alcohol were obtained, which by its density corresponded to 45 grammes of absolute alcohol. This weight amounts to three-fourths of the olefiant gas absorbed: the rest was lost in the several manipulations.

The alcohol thus obtained exhibited all the characters of ordinary alcohol produced by fermentation, having a spirituous taste and odour, distilling without residue at 79° to 81° C., yielding olefiant

gas when heated with sulphuric acid, and acetic ether when distilled with sulphuric and acetic acids together.

To obtain further confirmation of this result, olefiant gas obtained by the action of hydrochloric acid and mercury on the iodide of ethylene ($C_2H_4I_2 + 4Hg = C_2H_4 + 2Hg_2I$), was absorbed by sulphuric acid, and the liquid saturated with carbonate of baryta or carbonate of lime; in this manner the sulphovinates were obtained.

The baryta-salt distilled with acetate of soda yielded acetic ether; with butyrate of potash, butyric ether; and with benzoate of potash, benzoic ether, $C_{14}H_{10}O_4, C_4H_4$. This latter product boiled at $210^\circ C.$, and yielded benzoic acid and alcohol when treated with potash.

Lastly, to show that the same results may be obtained with olefiant gas not originally derived from alcohol, coal-gas was subjected to the action of iodine, and the resulting iodide of ethylene decomposed by heating it with potash. The pure olefiant gas thence obtained was absorbed by sulphuric acid as before, and by the series of operations above described, benzoic ether was obtained, which when distilled with potash, yielded benzoic acid and alcohol. This is the first time that alcohol has been produced without fermentation.

Formation of Propylic Alcohol, $C_6H_8O_2$, from Propylene, C_6H_6 .
—Propylene gas is absorbed by strong sulphuric acid almost as rapidly as carbonic acid by potash; and on subsequently diluting the acid with water, filtering, and distilling, propylic alcohol is obtained in the form of a spirituous liquid, having a peculiar pungent odour, soluble in water, but precipitated from the solution by carbonate of potash. This liquid in a state of concentration, but still mixed with a certain quantity of water, has a density of 0.817, and begins to boil at 81° to $82^\circ C.$ It mixes in all proportions with water, and forms with crystallised chloride of calcium either a homogeneous solution, or two distinct strata, according to the proportion of the salt. It burns with a brighter flame than common alcohol; mixed with sulphuric acid and sand, and heated, it blackens, decomposes rapidly, and yields propylene-gas, mixed with about $\frac{1}{10}$ th of another combustible gas, probably hydride of propyl, C_6H_8 . Distilled with a mixture of sulphuric and butyric acids, it yields *propylo-butyric ether*, $C_8H_8O_4, C_6H_6$, which is a neutral liquid, lighter than water, volatile below $130^\circ C.$, and having an odour like that of butyric ether, but more unpleasant; it is decomposed at 100° by potash, yielding butyrate of potash and propylic alcohol. The alcohol distilled with sulphuric and acetic acid, yields propylacetic ether, analogous to ordinary acetic ether, but volatilising at about $90^\circ C.$ A mixture of propylic alcohol and sulphuric acid, gently heated, and then saturated with carbonate of baryta, yields a crystallisable salt, the sulphopropylate of baryta, $S_2O_6, C_6H_6, HO, BaO + 6 Aq.$ This salt parts with its water of crystallisation in vacuo. With benzoate of potash, it forms propylo-

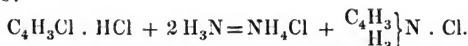
benzoic ether. By immediately saturating with carbonate of baryta the solution of propylene in sulphuric acid, two salts were obtained, containing different quantities of water, viz. $S_2O_6, C_6H_6, HO, BaO + 6 Aq.$ identical with the salt obtained from propylic alcohol, $S_2O_6, C_6H, HO, BaO + 2 Aq.$, corresponding with the sulphovinate. These two, hydrates exhibit the same degree of stability, and behave in the same manner with various salts, both producing the acetate, butyrate, and benzoate of propyl.*

Propylene is likewise absorbed by hydrochloric acid. When this gas is left to stand at ordinary temperatures over a stratum of the fuming acid, it is slowly taken up and disappears after some weeks: this reaction takes place even in a sealed tube. At $100^\circ C.$ the absorption is complete in 30 hours. The product is a neutral liquid, lighter than water, and insoluble in that fluid. After being purified with potash and distilled, it consists for the most part of hydrochlorate of propylene, C_6H_6, HCl , which volatilises at about $40^\circ C.$, and has the odour, taste, and flame of hydrochloric ether.

On the Substitution of the Aldehyde Radicals in Ammonia.†

By J. Natanson.

Oxide of Acetylammonium: $C_4H_3 \left\{ \begin{smallmatrix} H_3 \\ H_3 \end{smallmatrix} \right\} NO . HO$.—This compound, or rather the corresponding chloride, is obtained by the action of chloride of ethylene ($C_4H_4Cl_2$ or $C_4H_3Cl . HCl$) on ammonia at high temperatures:—



When one part of chloride of ethylene and five parts of strong ammonia are placed together in a sealed tube and heated in an oil-bath to 150° (no action takes place at 100°), the chloride of ethylene is completely absorbed in the course of a few hours, and the whole converted into a homogeneous yellow, watery, liquid. On opening the tube, the odour of chloride of ethylene is no longer perceptible; and if the liquid be left to evaporate over sulphuric acid or in a warm place, sal-ammoniac separates out, and a mother-liquid is obtained which yields nothing but water and ammonia by distillation with hydrate of lime, and therefore does not appear to contain any volatile organic base; but on treating it with recently precipitated oxide of silver, evaporating

* The compound formed with propylene and fuming sulphuric acid does not reproduce these ethers.

† Ann. Ch. Pharm. xcii. 48.

the filtrate to dryness at a gentle heat to expel the ammonia, and extracting the residue with water, a solution is obtained having a strong alkaline reaction, and therefore indicating the presence of a *non-volatile base*. The aqueous solution blackened on exposure to the air, and deposited reduced silver; and on removing the silver by sulphuretted hydrogen, expelling the excess of that gas from the filtrate by heat, neutralising the remaining liquid with sulphuric acid, decomposing the sulphate with caustic baryta (taking care to avoid an excess of that reagent) and extracting with alcohol, the base was obtained in the free state.

Great difficulty was experienced in fixing the composition of this base by analysis, because none of its salts could be made to crystallise, the only mode of obtaining them in a state approaching to purity being to precipitate them from their aqueous solutions by alcohol. They are then obtained in the form of white flocculent precipitates, which in drying aggregate together in yellow viscid masses, rendering it impossible to dry them completely; moreover, in the dry state they are highly hygroscopic.

The sulphate prepared in the manner just described, gave, in two analyses, 40.77 and 41.13 per cent. sulphuric acid; the formula $\begin{matrix} \text{C}_4\text{H}_3 \\ \text{H}_3 \end{matrix} \} \text{NO} \cdot \text{SO}_3$ requires 43.47. The chloroplatinate, which, ac-

ording to the formula, $\begin{matrix} \text{C}_4\text{H}_3 \\ \text{H}_3 \end{matrix} \} \text{NCl} \cdot \text{PtCl}_2$ should contain 39.57 per cent. platinum, yielded only 38.22 per cent. These results not being sufficiently accurate to establish the formula without further confirmation, such confirmation was sought in the proportion of carbonic acid and nitrogen obtained by combustion of the sulphate. Experiment gave $\text{N} : \text{CO}_2 = 1 : 3.91$, which does not differ much from the ratio given by calculation, viz. 1 : 4. These results, viewed in connection with the two following reactions, which show that the base contains the radical of aldehyde, may be regarded as sufficient evidence that it is really the *oxide of acetylammonium*.—1. When nitrate of silver is added to a solution of the chloride and the liquid heated, aldehyde is copiously evolved, especially if a few drops of dilute sulphuric acid be added:— $\begin{matrix} \text{C}_4\text{H}_3 \\ \text{H}_3 \end{matrix} \} \text{NO} + \text{NO}_3 = \text{C}_4\text{H}_3\text{O} \cdot \text{HO} + 2\text{N} + 2\text{HO}$.

2. When ammonia and nitrate of silver are added to a solution of the base or of either of its salts, and the liquid boiled for some time, an extremely beautiful specular deposit of silver is formed, indicating the presence of a considerable quantity of aldehyde-ammonia. This reaction is slower with the chloride than with other salts, because the separated chloride of silver is difficult to reduce.

The base separated from the sulphate by means of baryta forms a yellowish, inodorous, viscid mass, which dissolves readily in water and

alcohol. The aqueous solution has a strong alkaline reaction, a slightly caustic taste, and when boiled gives off the faint characteristic odour of alkaline solutions. It easily expels ammonia from ammoniacal salts. It absorbs carbonic acid from the air, and afterwards effervesces with acids. When heated it becomes carbonised, giving off vapours which have a faint but characteristic odour. When aqueous ethylamine is added at ordinary temperatures to a salt of acetylammonium, its odour is immediately destroyed, a proof that ethylamine separates acetylamine from its compounds; on boiling, however, the ethylamine is expelled, its volatility then coming into play. Hydrated oxide of acetylammonium does not dissolve alumina; it dissolves oxide of silver with great facility, but the silver is quickly reduced on heating the liquid. Solution of chloride of gold produces an orange-yellow amorphous precipitate, which dissolves readily when the liquor is heated, but is almost simultaneously decomposed, with reduction of gold. Bichloride of platinum forms a deep orange-yellow filmy precipitate, which afterwards aggregates together. Chloride of mercury forms a white precipitate very sparingly soluble in cold water, but dissolving with tolerable facility in hot water, and separating out again on cooling; it is insoluble in alcohol.

Sulphate of acetylammonium is precipitated from a moderately concentrated aqueous solution by alcohol in white flakes; from a stronger solution, as a non-miscible yellow stratum of liquid. It has a slight acid reaction, even if the aqueous solution before precipitation with alcohol has been made alkaline by excess of base. When dried, it forms a viscid, yellow mass.

The *nitrate* is similar to the sulphate. The *oxalate* is precipitated by alcohol from the aqueous solution in the form of a white gelatinous precipitate, which, if the solution is concentrated, converts the liquid into a pasty mass. The aqueous solution of the *chloride* does not mix in the concentrated state with alcohol, but remains as a heavy stratum at the bottom; but in the dilute state, the chloride, unlike the other salts, is not precipitated by alcohol. The salts of acetylammonium are very hygroscopic, becoming moist in a few seconds after drying. They are all insoluble in ether:

Hydrated oxide of acetylammonium, $\left. \begin{matrix} \text{C}_4\text{H}_3\text{N} \\ \text{H}_3 \end{matrix} \right\} \text{NO} \cdot \text{HO}$, is isomeric with aldehyde ammonia $\text{C}_4\text{H}_4\text{O}_2 \cdot \text{H}_3\text{N}$; and though it has certain properties in common with that compound, *e. g.* the reaction with silver-salts, it is nevertheless sufficiently distinguished therefrom by its fixity, its basic qualities, and its permanency in presence of acids and alkalis. The most remarkable and interesting point connected with this base is its non-volatility. It is, in fact, a fixed alkali, like the bases of Hofmann's fourth series; and though much less complex than those bases, is nevertheless permanent at ordinary

temperatures, and is not resolved into water and acetylamine, even when heated. Its existence affords one more argument in favour of the ammonium-theory, tending in fact to show that the ammonium-oxides are the true bases, while ammonia and the compound ammonias are merely products resulting from their decomposition.

It is very probable that by treating the aqueous solution of oxide of acetylammionium with fresh quantities of chloride of ethylene, a greater number of equivalents of hydrogen may be replaced by acetyl, and that by treating it with alcohol-radicals, a series of new fixed alkaloids may be formed.

Investigations in the same directions as those of Natanson above described, but with somewhat different results, have been made by Cloez.* This chemist has examined the action of ammonia in the state of alcoholic solution on bromide of ethylene, $C_2H_4Br_2$ or $C_2H_3Br \cdot HBr$. He finds that these bodies do not act upon another in the cold, but that, when the mixture is enclosed in sealed tubes and heated for two or three hours in boiling water, a copious deposit of bromide of ammonium is formed, which increases on cooling. The action is completed in twelve hours; and if the ammoniacal liquid be then filtered from the saline deposit and evaporated, there remains a solid deliquescent residue, which, when heated with a mixture of lime and potash, gives off, first a very caustic transparent liquid having a decided ammoniacal odour, afterwards a viscid, and at last a thick glutinous liquid. If the distillate be left for twenty-four hours in contact with fused caustic potash, and then rectified, about one-third passes over between 140° and 145° C., the rest at a temperature above 350° . The more volatile portion is a transparent colourless liquid, having a faint ammoniacal odour and very caustic taste; it has an alkaline reaction, neutralises acids, and forms with them salts, most of which crystallise readily. The formula of this base is C_2H_3N . Cloez calls it *Formiline* (better perhaps *Formylamine*), inasmuch as it may be regarded as ammonia in which 1 eq. H is replaced by 1 eq. formyl, C_2H . Formylamine acts, even at ordinary temperatures, upon the bromides of methyl, ethyl, and amyl, forming new liquid bases, whose composition may easily be predicted.

The crude product from which the formylamine has been distilled yields a second base which boils at 200° , and is regarded by Cloez as *Acetyliac* or *Acetylamine*, although the analyses which have been made of it do not establish the formula very precisely.

* Institut, 1853, 213; Liebig and Kopp's Jahresbericht, 1853, 468.

Compounds of the Ketones with Alkaline Bisulphites.***By Dr. Limpricht.**

THE Ketones form with alkaline bisulphites crystalline compounds similar to those which Bertagnini has obtained with the aldehydes.

1. Pure acetone, agitated with a concentrated solution of bisulphite of soda, dissolves with considerable evolution of heat, and the liquid on cooling yields laminæ of the sulphite of acetone and soda. These crystals dissolve pretty easily in water, less readily in alcohol; when they are heated alone, empyreumatic products are evolved; on distilling them with an alkaline carbonate, pure acetone passes over. For analysis, they were freed from the mother-liquor by pressure between paper, and dried over sulphuric acid:—

		Calculated.	Found.
6 C . . .	36	22·2	21·3
7 H . . .	7	4·3	4·1
3 O . . .	24	14·8	15·7
NaO . . .	31	19·1	19·2
2 SO ₂ . . .	64	39·6	39·7
<hr/>			
NaO . C ₆ H ₆ O ₂ . 2SO ₂ + Aq.	162	100·0	100·0

2. The compound of acetone with bisulphite of potash is prepared like the soda-compound, and resembles it in all its properties. It gave by analysis 27·21 per cent. of potash, agreeing very nearly with the formula $\text{KO} \cdot \text{C}_6\text{H}_6\text{O}_2 \cdot 2\text{SO}_2$, which requires 27·81 per cent.

3. When acetone is mixed with a very strong solution of bisulphite of ammonia, it dissolves with so great a rise of temperature, that the mixture begins to boil; nevertheless, it does not deposit any crystals on cooling. After evaporation, the compound remains in the solid form, but still mixed with bisulphite of ammonia. The author has not yet obtained it in the pure state.

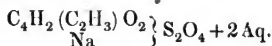
Sulphite of acetone and ammonia distilled with excess of lime (as in Gössmann's process, see page 160) yields a volatile base, which may be separated from the ammonia that passes over with it by treating the dry hydrochlorates with absolute alcohol. When the salt which remains on evaporating the alcoholic solution is treated with potash, a strong ammoniacal odour is evolved, and an inflammable vapour given off.

By agitating a concentrated solution of an alkaline bisulphite with the liquid containing butyral and butyrene obtained by distilling butyrate of lime, or with the mixture of valeral and valerone produced in a similar manner from valerate of lime, results were obtained showing, first, that butyrene and valerone behave with alkaline

* Ann. Ch. Pharm. xciii. 238.

bisulphites in the same manner as acetone, and consequently, that the same may very probably be predicted of all ketones; secondly, that butyral and valeral, which, on account of their boiling-points and their reaction with ammonia, have been regarded as not identical with the aldehydes of butyric and valerianic acids, at least resemble the aldehydes in their behaviour with alkaline bisulphites.

The compounds of ketones with alkaline bisulphites may, perhaps, throw some light on their rational formulæ. Gerhardt derives the aldehydes from the type hydrogen $\begin{smallmatrix} \text{H} \\ \text{H} \end{smallmatrix}$, by substituting 1 atom of the oxygen-radical of the corresponding acid (othyl or acetyl $\text{C}_4\text{H}_3\text{O}_2$, for example, in the case of acetic acid) for 1 atom hydrogen: thus, common aldehyde = $\begin{smallmatrix} \text{C}_4\text{H}_3\text{O}_2 \\ \text{H} \end{smallmatrix}$. Now, in the compounds of the aldehydes with alkaline bisulphites, the other atom of hydrogen is replaced by the alkali-metal: *e. g.* $\begin{smallmatrix} \text{C}_4\text{H}_3\text{O}_2 \\ \text{K} \end{smallmatrix} \} \text{S}_2\text{O}_4$. The ketones are derived from the same type, and are regarded as aldehydes, in which the second atom of hydrogen is replaced by an alcohol-radical, thus: acetone = $\begin{smallmatrix} \text{C}_4\text{H}_3\text{O}_2 \\ \text{C}_2\text{H}_3 \end{smallmatrix}$. This mode of representation, however, does not explain the formation of compounds of ketones with the alkaline bisulphites, because the place of the atom of hydrogen, which should be replaced by the alkali-metal, is already occupied by an alcohol-radical. But if the formula of acetone be written thus, $\begin{smallmatrix} \text{C}_4\text{H}_2(\text{C}_2\text{H}_3\text{O}_2) \\ \text{H} \end{smallmatrix} \}$, which amounts to supposing that an atom of hydrogen in the oxygen-radical itself is replaced by methyl (as in gaultheria-oil), the difficulty just mentioned will be removed, and the rational formula of sulphite of acetone and soda will be—



On Caprylic Aldehyde.*

By Dr. Limpricht.

THE liquid product obtained by distilling castor-oil or its soaps with hydrate of potash, is stated by Bouis,† Cahours,‡ Moschnin,§ and Squire,|| to be caprylic alcohol, $\text{C}_{16}\text{H}_{18}\text{O}_2$; Wills and Railton,¶

* Ann. Ch. Pharm. xciii. 242.

† Compt. rend. xxxviii. 935; Ann. Ch. Phys. [3] xlv. 77; Chem. Soc. Qu. J. vii. 286.

‡ Compt. rend. xxxix. 254.

§ Ann. Ch. Pharm. lxxvii. 111.

|| Chem. Soc. Qu. J. vii. 108.

¶ Ibid. vi. 208, 307.

on the other hand, regard it as α -nanthylic alcohol, $C_{14}H_{16}O_2$. According to Limpricht, however, it is not an alcohol at all, but caprylic aldehyde, $C_{16}H_{16}O_2$. This conclusion is based on the fact that the liquid in question, when mixed with a concentrated solution of bisulphate of potash or soda, yields a large quantity of a crystalline compound (a property belonging to the aldehydes and acetones, but not to the alcohols); and that this compound, when freed from the mother-liquor by pressure between paper, washed with cold alcohol, dried over sulphuric acid, and then dissolved in hot water, yields pure caprylic aldehyde. In fact, the liquid thus obtained, after being dried over chloride of calcium, and rectified till it boiled constantly at 178° , yielded by analysis 74.65 (mean) per cent. of carbon, and 12.76 of hydrogen, numbers agreeing very nearly with the formula of caprylic aldehyde, which requires 75.0 per cent. carbon and 12.5 of hydrogen.

The crystalline compounds of this aldehyde cannot be purified by crystallisation; moreover, they undergo a slow spontaneous decomposition, continually giving off sulphurous acid: hence they are not well adapted for analysis. The potash-salt, when purified as completely as possible, exhibited too great a quantity of potash and too little sulphurous acid to agree with the formula, $C_{16}H_{15}O_2 \left\{ \begin{smallmatrix} K \\ S_2O_4 \end{smallmatrix} \right\} + 3Aq$; but the proportions of carbon and hydrogen found by combustion agreed very closely with that formula.

Caprylic aldehyde turns acid on exposure to the air, like other aldehydes,—a fact which explains the result obtained by Railton, who, by passing oxygen gas through his supposed α -nanthylic alcohol, obtained a large quantity of acid.

[The experiments just described certainly show that caprylic aldehyde occurs among the products of the distillation of castor-oil with hydrate of potash, and that it may be separated out by combination with alkaline bisulphites; but they by no means prove that it is the only product. On the other hand, the very exact analytical results obtained by Bouis, and the numerous derived compounds obtained by himself and others, establish beyond doubt that caprylic alcohol is not only a product, but one of the chief products of the decomposition; and the experiments of Wills and Railton also render it probable that α -nanthylic alcohol is sometimes obtained by the same process.—ED.]

Chemical Notices.*

By H. Limpricht.

1. *Preparation of Leucin from the Aldehyde of Valerianic Acid.*—The reaction on which this mode of preparing leucin depends is similar to that by which Strecker obtained alanine from the aldehyde of acetic acid. The ammoniacal compound of valeral is boiled in a retort with hydrocyanic and hydrochloric acid, till the oily layer, consisting of the fused ammonia-compound, has completely disappeared. The greater part of the sal-ammoniac is then left to crystallise out; the hydrochloric acid removed by hydrated oxide of lead; the lead by sulphuretted hydrogen; and lastly, the residue which remains after evaporating the filtrate, crystallised from hot dilute alcohol. The laminæ thus obtained exhibit the reaction and composition of leucin, viz. :—

		Calculated.	Found.
12 C	. . .	72	54.9
13 H	. . .	13	9.9
N	. . .	14	10.7
4 O	. . .	32	24.5
<hr/> C ₁₂ H ₁₃ NO ₄ <hr/>		<hr/> 131 <hr/>	<hr/> 100.0 <hr/>

2. *On the Metaldehyde of Valerianic Acid.*—It is stated by Parkinson,† that an isomeric modification of valeral is obtained, (1) in the preparation of that body by the action of sulphuric acid and chromate of potash on fusel-oil; (2) when valeral is heated above its boiling point; (3) by heating the sulphite of valeral and soda with dry carbonate of soda. According to Limpricht, however, no such modification is obtained by either of these processes.

3. *Easy Method of Preparing Chloride of Ethylene.*—A tubulated retort is half filled with a mixture of 2 parts black oxide of manganese, 3 parts common salt, 4 parts water, and 5 parts sulphuric acid, and loosely connected with a flask to serve as receiver. Olefiant gas is then passed into the mixture by means of a tube passing through the cork of the tubulure, and dipping half an inch below the surface of the liquid. So long as the gas is passing through the mixture, the retort must be only very gently heated,—as by placing under it a single red-hot coal,—and the resulting chloride of ethylene afterwards distilled over at a higher temperature. If this precaution be attended to in heating the chlorine-mixture, the operator will not be annoyed by escape of chlorine.

Where coal-gas is at hand, it will naturally furnish the readiest

* Ann. Ch. Pharm. xciv. 243.

† Ibid. xc. 114.

source of ethylene; but when that is not the case, the olefiant gas may be readily prepared from alcohol and sulphuric acid, by adopting Wöhler's method of adding sand to the mixture in sufficient quantity to make it into a thick paste, this addition completely preventing the frothing which otherwise causes so much inconvenience. The crude product thus obtained in an hour and a half from 2 ounces of alcohol yielded 1 ounce of pure chloride of ethylene.

The arrangement just described is peculiarly well adapted for condensing the gases homologous with ethylene, when it is desired to submit them to further examination, for which purpose they were formerly collected in gasometers over water, and converted into liquid bromides by contact with bromine. If, for example, we wish to examine the hydrocarbons homologous with ethylene, which are obtained by heating valerate of baryta, the retort containing that salt may be connected air-tight with a tubulated and well-cooled receiver to condense the liquid products, and the gases not condensed in the receiver made to pass into the chlorine-mixture.

4. The following compounds, usually regarded as aldehydes and ketones, do not combine with alkaline bisulphites, either when agitated and heated with an aqueous solution of the potash or soda-salt, or when their alcoholic solution is mixed with an alcoholic solution of the ammonia-salt.

Myristone, prepared by dry distillation of myristate of lime; a mixture of *Palmitone* and *Stearone*, obtained by quickly heating margaric acid with excess of lime; *Benzophenone*, prepared in a similar manner from benzoate of lime; *Phorone*, from camphorate of lime; *Palmitic aldehyde*, obtained by oxidising ethal with a mixture of chromate of potash and sulphuric acid.

Hence it appears that the property of combining with alkaline bisulphites does not belong to all aldehydes and ketones,—or, perhaps, the bodies just mentioned do not belong to either of these groups.

On Compound Ureas.

By N. Zinin* and F. Moldenhauer.†

THE researches of Chancel, Wurtz, and Hofmann, have brought to light a number of compounds which may be regarded as urea, in

* J. pr. Chem. lxii. 355, Ann. Ch. Phys. [3] xlv. 57.

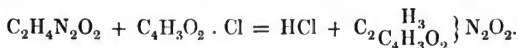
† Ann. Ch. Pharm. xciv. 100. The experiments of Zinin and Moldenhauer appear to have been made about the same time and independently of each other. Zinin's paper, however, was published first, containing a full description of the acetyl and benzoyl ureas, and a slight notice of the other two compounds. The description and analysis of these latter is due to Moldenhauer.

which one or more equivalents of hydrogen are replaced by a corresponding number of equivalents of a hydrocarbon. The following experiments show in like manner that the hydrogen in urea may be replaced by oxygen-radicals :—

1. *Acetureid, Acetyl-urea, or Othyl-urea*, $C_2 \overset{H_3}{C_4H_3O_2} \} N_2O_2$. —

When chloride of othyl, $C_4H_3O_2 \cdot Cl$, is poured upon dry urea, the action commences immediately; the mixture becomes spontaneously heated; the chloride of othyl volatilises; and the liquid is gradually converted into a white viscous mass. When this substance is kept for some minutes at a temperature of $120^\circ C$., it loses altogether the odour of chloride of othyl, and if treated with ether after cooling, does not yield anything to that solvent. The residue dissolved in hot alcohol crystallises from that solution in long needles with rectangular base, generally striated, and having a bright white colour and silky lustre. One part of this body dissolves in 10 parts of boiling alcohol, but requires 100 parts of cold alcohol to dissolve it. Hot water dissolves it more readily than alcohol, and deposits it on cooling in stellate groups of prisms with rhomboidal bases and dihedral summits.

In the formation of this compound, the reaction takes place between 1 eq. of chloride of othyl and 1 eq. urea :—



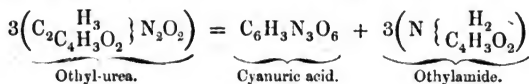
An excess of urea appears, however, to be advantageous in the preparation. According to Zinin, the best proportions are 2 eq. urea to 1 eq. chloride of othyl.

The composition of othyl-urea is as follows :—

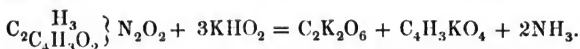
		Calculated.	Zinin.	Moldenhauer.
6 C . . .	36	35.29	35.56	35.29
6 H . . .	6	5.88	5.92	5.88
2 N . . .	28	27.45	27.05	
4 O . . .	32	31.38	31.47	
<hr/> C ₆ H ₆ N ₂ O ₄ <hr/>	<hr/> 102 <hr/>	<hr/> 100.00 <hr/>	<hr/> 100.00 <hr/>	

When othyl-urea is heated on platinum-foil, white vapours are evolved, and the crystals become covered with a woolly sublimate. At a higher temperature, the whole volatilises. When it is heated in a tube, the sublimate makes its appearance at $160^\circ C$., and at 200° the substance melts to a transparent liquid, which on evaporation is converted into a crystalline mass soluble in water and alcohol. The spirituous solution yields by evaporation, crystalline nodules composed

of thick shortened rhomboidal prisms. At a still higher temperature, othyl-urea is resolved into othylamide and cyanuric acid :—



Potash decomposes othyl-urea into carbonic acid, acetic acid, and ammonia.



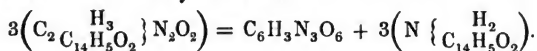
2. *Butyryl-urea*, $\text{C}_{10}\text{H}_{10}\text{N}_2\text{O}_4 = \text{C}_2\text{C}_8\overset{\text{H}_3}{\text{H}_7}\text{O}_2\text{N}_2\text{O}_2$; obtained like the preceding by the action of chloride of butyryl on urea. Crystallises readily from water in small crystalline scales; from alcohol in very thin, somewhat elongated, highly lustrous laminæ, which appear to belong to the rhombic system. It is inodorous and tasteless, and melts at 176° to a yellowish liquid, which solidifies again in the crystalline form on cooling; at a high temperature, it decomposes like othyl-urea. This compound in the state of aqueous solution is not precipitated either by nitric and oxalic acid, or by mercuric nitrate. The mean of two analyses gave 45.68 per cent. of carbon and 7.53 hydrogen; the formula requires 46.15 C., and 7.69 H.

3. *Valeryl-urea*, $\text{C}_{12}\text{H}_{12}\text{N}_2\text{O}_4 = \text{C}_2\text{C}_{10}\overset{\text{H}_3}{\text{H}_9}\text{O}_2\text{N}_2\text{O}_2$. — Obtained by the action of chloride of valeryl on urea.* It is nearly insoluble in cold water and alcohol. From the hot aqueous solution it is deposited in microscopic laminæ, having a pearly lustre, and soft and unctuous to the touch, the alcoholic solution yields thin needles, which, under the microscope, appear like transparent four-sided prisms. It melts at 191°C. , and when carefully heated in a tube, yields a crystalline sublimate of broad iridescent laminæ. Analysis gave 49.57 per cent. carbon; and 8.79 hydrogen; the formula requires 50.00 C., and 8.33 H.

4. *Benzoyl-urea*, $\text{C}_{16}\text{H}_8\text{N}_2\text{O}_4 = \text{C}_2\text{C}_{14}\overset{\text{H}_3}{\text{H}_3}\text{O}_2\text{N}_2\text{O}_2$. — This body is obtained by heating a mixture of 2 eq. urea and 1 eq. chloride of benzoyl in an oil-bath to 150 or 155° , care being taken that the temperature, which increases as soon as the action commences, does not rise above 160° : for this reason it is best not to operate on more than 12 or 15 grammes at once. On treating the cooled and pulverised mass

* Chloride of valeryl, not previously known, was obtained by the action of oxychloride of phosphorus on valerate of soda. It is a colourless, very mobile liquid, which fumes strongly in the air, and is resolved by water into hydrochloric and valerianic acids (Moldenhauer).

with cold alcohol, hydrochloric acid and the excess of urea dissolve, and there remains a crystalline powder, which, when dissolved in boiling alcohol, yields, on cooling, thin rectangular laminæ of benzoyl-urea, often with pointed summits. These crystals are very brilliant, and resemble those of benzoic acid, but are distinguished therefrom by their solubility in alcohol. One part of benzoyl-urea dissolves in 10 parts of boiling and 100 parts of cold alcohol; in water and ether it is still less soluble. Hot hydrochloric acid dissolves the crystals without alteration, and deposits them on cooling. Nitric acid decomposes benzoyl-urea, with formation of benzoic acid. Ammonia does not alter it. Potash dissolves it in the cold, and decomposes it at a boiling heat, with evolution of ammonia. Heated in a tube to 200° C. it melts, without alteration of weight, into a colourless liquid, which on cooling solidifies in a crystalline mass, having the same composition as benzoyl-urea, but different properties, dissolving more readily in water, and crystallising differently. Benzoyl-urea heated above its melting point froths up, becomes filled with crystals of benzamide, and leaves a residue of cyanuric acid:—



On a new Mode of Formation of Ethylamine, Amarine, and Lophine.*

By A. Gössmann.

1. *Ethylamine*.—When bisulphite of aldehyde-ammonia is heated with lime, ethylamine is evolved, and the sulphurous acid is converted into sulphuric acid:—



To obtain ethylamine by this decomposition, it is by no means necessary to go through the troublesome process of preparing crystallised aldehyde-ammonia; it is sufficient to take the crude distillate containing aldehyde, which is obtained by acting on alcohol with sulphuric acid and peroxide of manganese (or bichromate of potash); mix it with the requisite quantity of bisulphite of ammonia; evaporate to dryness; mix the perfectly dry saline mass with four times its weight of a mixture of quick and slaked lime; and distil it in a retort provided with a bent tube for conveying the evolved gas into dilute hydrochloric acid. The distillation must be performed immediately after the mixture is made, and the mass must be heated as quickly and as strongly as possible; otherwise aldehyde and ammonia pass over: the latter is always evolved when an excess of bisulphite of ammonia has been

* Ann. Ch. Pharm. xci. 122; xciii. 329.

added. The sal-ammoniac thus formed is, however, easily removed by a mixture of alcohol and ether, which dissolves the hydrochlorate of ethylamine, but leaves the sal-ammoniac undissolved.

2. *Formation of Amarine and Lophine*.—Since, as shown by Bertagnini, it is a general property of aldehydes to unite with alkaline bisulphites, producing compounds similar to that formed by ordinary aldehyde, it appeared probable that they would also, when treated in the manner just described, yield organic bases. This expectation has been verified with regard to bitter almond oil. The sulphurous acid compound was prepared by mixing a concentrated alcoholic solution of acid sulphite of ammonia with a sufficient quantity of bitter almond oil, collecting the resulting crystalline mass after it had ceased to increase in quantity, and drying it. The perfectly dried mass was then mixed with three or four times its volume of very dry and recently prepared hydrate of lime; the mixture introduced into a capacious retort, and covered with a thin layer of lime; and the retort, after being connected with a well-cooled receiver, was surrounded as quickly as possible with hot coals, and heated to 180° — 200° C. The cool part of the neck of the retort then immediately became covered with a white amorphous-looking mass, which, as the heat increased, ran down into the receiver in oily drops. This substance is *amarine*. The heating was continued as long as oily striæ appeared in the neck of the retort, and the sublimate in the hottest part of it continued to increase.

When the operation is properly conducted, the amarine is found, partly in the receiver, suspended in an ammoniacal liquid rendered turbid by the presence of a small quantity of bitter almond oil, partly in the lower part of the neck of the retort. In the upper part there is always found another substance, partly detached in tuft-like groups of needles, partly coating the glass in radiating masses. This second body is *Lophine*.

To collect the amarine, and separate it from a small quantity of oily products, it is rinsed into the receiver with a small quantity of cold alcohol, dissolved by addition of alcohol and hydrochloric acid, precipitated by ammonia, and purified by recrystallisation and treatment with animal charcoal. The hydrochlorate of this base yielded the following results by analysis:—

	Calculated.	Found.
42 C . . . 292.0	75.33	75.15
19 H . . . 19.0	5.68	5.62
2 N . . . 28.0	8.37	
Cl . . . 35.5	10.62	
<hr/> C ₄₂ H ₁₈ N ₂ . HCl	<hr/> 374.5	<hr/> 100.00

The chloroplatinate left on ignition 19·8 per cent. of platinum ; the formula $C_{42}H_{19}N_2Cl \cdot PtCl_2$ requires 19·58 per cent.

The lophine which collected in the upper part of the retort and of its neck, was dissolved in hot alcohol, treated with animal charcoal, and recrystallised. It was in most cases so pure that, after one recrystallisation, it exhibited the appearance of dazzling white needles. It melted at $265^\circ C$, volatilising at the same time unchanged, and solidifying on cooling in a beautiful radiated mass. Its composition is as follows :—

		Calculated.	Found.
46 C	. . 276	85·98	85·69
17 H	. . 17	5·30	5·5
2 N	. . 28	8·72	
<hr/> C ₄₆ H ₁₇ N ₂	<hr/> 321	<hr/> 100·00	

The *chloroplatinate* left after ignition 18·89 per cent. of platinum ; the formula $C_{48}H_{18}N_2Cl \cdot PtCl_2$ requires 18·72 per cent.

The formation of lophine begins only when the retort has attained a very high temperature, and probably arises from the amarine formed in the interior of the mass not being able to escape before the temperature of the outer parts has risen high enough to decompose it. It may, therefore, be greatly promoted by using a capacious retort, heating it very strongly and suddenly, and covering the upper part immediately with red-hot coals, beginning from the front, so as to fulfil as quickly as possible all the conditions which are essential to cause the amarine to pass through a strongly heated space. By attending to these directions, needles of lophine more than an inch long may be obtained, even with small quantities of material.

In the preparation of amarine and lophine, as in that of ethylamine, it is not absolutely necessary first to prepare the crystallised compound of the aldehyde with acid sulphite of ammonia ; it is sufficient to mix a highly concentrated solution of acid sulphite of ammonia with the corresponding quantity of bitter almond oil dissolved in a little alcohol ; evaporate to dryness as quickly as possible over the water-bath ; and mix the resulting mass immediately with recently prepared and perfectly dry hydrate of lime : if the mass be used before it is thoroughly dry, or if the hydrate of lime be very moist, the compound is for the most part resolved, during the distillation, into ammonia and bitter almond oil. As, however, this mode of proceeding always gives rise to the formation of a certain quantity of benzoic acid in the mass, a quantity of benzol corresponding to this admixture of benzoic acid is always found in the distillate ; an impurity, however, which is not very difficult to remove, inasmuch as it volatilises very quickly when the product of the distillation is heated to 80° or $90^\circ C$.

On Telluromethyl.*

By F. Wöhler and J. Dean.

THIS compound is obtained by a process exactly similar to that which is adopted for the preparation of tellurethyl,† namely, by distilling telluride of potassium with a tolerably strong solution of sulphomethylate of baryta: the reaction goes on very easily. The distillation was continued as long as drops of oil continued to pass over with the water.

Telluromethyl is a pale yellow, mobile liquid, which sinks in water, and does not mix with it. Its odour is extremely unpleasant, like that of garlic, very intense, and so persistent that even the breath of the operator becomes affected by it. It was found to boil at $82^{\circ}\text{C}.$ ‡ Its vapour is yellow, like that of tellurium itself. It fumes slightly in the air from oxidation. When set on fire, it burns with a light bluish white flame, giving off a thick vapour of tellurous acid.

Telluromethyl, $\text{C}_2\text{H}_3\text{Te}$, like tellurethyl, has the chemical relations of a radical or metal. It forms a basic oxide and corresponding haloid compounds.

Oxide of Telluromethyl, $\text{C}_2\text{H}_3\text{TeO}$.—Formed by heating telluromethyl with moderately strong nitric acid. At first, a portion dissolves with reddish yellow colour; then suddenly a violent action takes place, nitric oxide is evolved, and a colourless solution is formed, containing *nitrate of telluromethyl*, which, on carefully evaporating the solution, is obtained in large colourless prisms. This salt dissolves readily in water and in alcohol; when heated, it decomposes with detonation. It is the material from which all the other compounds of telluromethyl are obtained. The *oxide*, however, is most conveniently prepared, not directly from the nitrate, but by decomposing the chloride or iodide with oxide of silver. Oxide of telluromethyl in the dried state is indistinctly crystalline. When exposed to the air, it deliquesces, like potash, and absorbs carbonic acid. It has a most nauseous taste, but is destitute of odour. Its solution exhibits a strong alkaline reaction with litmus paper. It is so strong an alkali that it separates ammonia from sal-ammoniac even at ordinary temperatures, and forms a blue precipitate with sulphate of copper. From its solution, sulphurous acid immediately throws down telluromethyl in the form of an oily, stinking liquid: hydrochloric acid precipitates the white chloride; hydriodic acid the red iodide.

* Ann. Ch. Pharm. xciii. 233.

† Ibid. lxxxiv. 79; Chem. Soc. Qu. J. vi. 40.

‡ The real boiling-point is probably 80° : for in the experiment the telluromethyl was covered with a thin layer of water, and the thermometer did not dip into it immediately, but into oil, in which the very thin tube containing the telluromethyl was immersed. If the boiling-point be 80° , that of tellurethyl, which has not yet been determined by experiment, must, according to Kopp's law, be 99° .

Sulphate of Telluromethyl, formed by directly saturating the base with the acid, crystallises in transparent cubes, very regular, and of considerable size. It dissolves readily in water, but is insoluble in alcohol. The oxalate, tartrate, acetate, and formate are easily soluble.

Chloride of Telluromethyl, C_2H_3TeCl , is formed as a thick white precipitate resembling chloride of lead, when hydrochloric acid is dropt into the solution of the nitrate. It redissolves when heated, and crystallises on cooling in long thin prisms, resembling corrosive sublimate. Melts at $97.5^\circ C.$, but appears not to be capable of volatilising completely without decomposition. Although it cannot be distilled with water, its solution has nevertheless a faint alliaceous odour when heated. It solidifies in a very distinctly crystalline form. Dissolves readily in alcohol. When prepared from the amorphous nitrate, it contains tellurous acid, either admixed or in combination. Does not form any precipitate with bichloride of platinum.

The *Oxychloride*, $C_2H_3TeCl + C_2H_3TeO$, is formed by dissolving the chloride in ammonia. The solution, when evaporated, yields a mixture of sal-ammoniac and the oxychloride, which may be separated by alcohol. The oxychloride forms short colourless prisms. Hydrochloric acid added to its solution precipitates the chloride.

Bromide of Telluromethyl, C_2H_3TeBr .—Produced like the chloride, to which it bears a strong resemblance, and with which it is probably isomorphous. Forms shining colourless prisms, and melts at $89^\circ C.$

Iodide of Telluromethyl.—Colourless hydriodic acid or solution of iodide of potassium dropped into a solution of nitrate or chloride of telluromethyl, forms a bright lemon-yellow precipitate, which after a while changes to vermilion-red. If the solutions are warm when mixed, the precipitate is immediately red and crystalline. After drying it forms a vermilion-coloured powder. The composition of the iodide is as follows:—

	Found.	Calculated.
Carbon	5.40	5.81
Hydrogen	1.61	1.45
Tellurium	31.24	31.12
Iodine	61.54	61.62
	<hr/> 99.79	<hr/> 100.00

Iodide of telluromethyl dissolves very sparingly in cold, much more readily in warm water. Hot alcohol dissolves it in large quantity, forming a reddish-yellow solution. From both solutions the iodide crystallises in small, shining, vermilion-coloured prisms, the alcoholic solution yielding the larger crystals. The crystals yield an orange-yellow powder. Under the microscope they appear orange-yellow by transmitted light, and certain faces exhibit a beautiful blue surface-colour.

When the cooled alcoholic solution is mixed with about an equal bulk of water, the iodide is thrown down as a lemon-yellow precipitate. But after a few minutes, a movement takes place among the particles, and in a short time the entire precipitate is converted into glimmering crystalline laminae of the colour of vermilion. Iodide of telluromethyl, therefore, like chloride of mercury, exhibits two states, a yellow and a red, connected most probably, as in the latter substance, with dimorphism. The yellow modification, however, has not yet been obtained in a fixed and crystalline form. The alcoholic solution, in which the iodide clearly exists in the yellow form, deposits it by spontaneous evaporation in red crystals; and it cannot be melted without decomposition, being converted into black iodide of tellurium, even at 130°C .

A solution of the oxide of telluromethyl dissolved in aqueous hydrocyanic acid did not yield any cyanogen compound, the base separating out quite unaltered when the liquid was evaporated.

When sulphuretted hydrogen is passed into a solution of chloride of telluromethyl, a white flocculent precipitate is formed. ($\text{C}_2\text{H}_3\text{TeS} + \text{C}_2\text{H}_3\text{TeCl}$?), which afterwards becomes yellowish, the liquid acquiring an intensely disgusting odour. If it be then distilled, there passes over with the water a very offensive, heavy, oily, reddish-yellow body, which, when oxidised with aqua-regia, yields sulphuric acid. When a solution of oxide of telluromethyl is saturated with sulphuretted hydrogen, a slight whitish turbidity is produced. On distilling the liquid, white sulphur separates out, as soon as the heat begins to act, and a yellow oil passes over, which appears to be merely reduced telluromethyl.

On Cuminal Alcohol.*

By C. Kraut.

GERHARDT and CAHOURS† have shown that the volatile oil contained in the seeds of *Cuminum Cyminum*, and known in commerce by the name of Roman cumin oil, is a mixture of two compounds, viz. a compound free from oxygen, called *Cymene*, and an oxygenised body called *Cuminol*. This latter substance is homologous with bitter almond oil, and stands in the same relation to cuminic acid as bitter almond oil to benzoic acid,—that is to say, it is the aldehyde of cuminic acid.

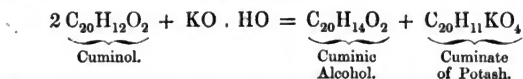
The two constituents of the Roman cumin-oil were separated by the following process:—After the whole of the cymene, together with a portion of the cuminol, had been removed from the commercial oil

* Ann. Ch. Pharm. xcii. 66.

† Ibid. xxxviii. 67.

by distillation at $200^{\circ}\text{C}.$, the residue was converted, by agitation with a concentrated solution of bisulphite of soda, into a crystalline double salt insoluble in saline solutions; this salt completely freed from the mother-liquor by pressure was then diffused in water, and the cuminol obtained from it in a state of purity by addition of carbonate of soda and distillation with vapour of water. The cuminol which had distilled over with the cymene was separated therefrom by agitation with solution of bisulphite of soda, so dilute that the resulting double salt remained in solution.

Cuminol becomes sensibly heated when mixed with several times its volume of a concentrated solution of hydrate of potash in alcohol; and if the mixture be kept for an hour in a state of ebullition, and regularly concentrated by allowing the condensed vapours to flow back again, the cuminol is completely decomposed, and there are formed, without any evolution of hydrogen, a large quantity of cuminate of potash, and two liquid compounds, cymene and cuminic alcohol, which, on addition of water, separate in the form of oil. Although these two bodies are always produced simultaneously, the author is disposed to think, from experiments hereafter to be described, and from the analogous behaviour of benzoic alcohol, that the cymene is formed, not from the cuminol, but by the action of potash on cuminic alcohol. On this supposition, the decomposition of cuminol by potash as above may be represented by the following equation:—



When the mixture, after being diluted with water, was distilled, the cuminic alcohol and the cymene passed over with the aqueous vapour; they were removed from the surface of the distillate; agitated with bisulphite of soda to free them from adhering cuminol; then dehydrated, and finally separated by fractional distillation.

The cuminic alcohol gave the following results by analysis:—

		Calculated.	Found.			
20 C . .	120	80.00	79.63	79.62	79.56	79.49
14 H . .	14	9.33	9.33	9.36	9.35	9.39
2 O . .	16	16.67				
<hr/>		<hr/>				
$\text{C}_{20}\text{H}_{14}\text{O}_2$	150	100.00				

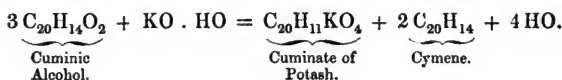
Cuminic alcohol is a colourless liquid, having a very faint but agreeably aromatic odour, and burning spicy taste; boils without decomposition at 243° , and does not turn acid, even by long exposure to the air. It is insoluble in water, but dissolves in all proportions

in alcohol and ether, and is not altered by agitation with solutions of alkaline bisulphites.

When heated with potassium, it gives off hydrogen and forms a solid granular mass, which is decomposed by water, yielding potash and cuminic alcohol. Strong nitric acid heated with cuminic alcohol converts it into cuminic acid, without the simultaneous formation of any other acids. Weaker nitric acid would probably first form cuminol. Concentrated sulphuric acid converts cuminic alcohol, without formation of any conjugated acid, into a resinous mass, which is brittle and friable when cold, but becomes semifluid when immersed in boiling water.

Of the compounds of cuminic alcohol corresponding to the compound ethers, only the benzoate has yet been examined. This compound is obtained by heating cuminic alcohol or its potassium-compound with chloride of benzoyl, and forms a buttery, indistinctly crystalline mass, which cannot be distilled without decomposition, is decomposed by potash-solution, even in the cold, and when washed merely with water, continually renders that liquid acid.

It has been assumed above that the formation of cymene from cuminol is due to the action of potash on the cuminic alcohol already formed. This assumption is supported by the fact that pure cuminic alcohol, when continuously boiled with alcoholic solution of potash, is decomposed in the manner denoted by the following equation:—



The cymene thus produced is identical with that which is formed by natural processes, and boils, like the latter, at $171\frac{1}{2}^{\circ}$ C. It gave the following results by analysis:—

		Calculated.	Found.	
20 C	. . 120	89.56	88.91	88.92
14 H	. . 14	10.44	11.01	10.62
<hr/>		<hr/>	<hr/>	
$\text{C}_{20}\text{H}_{14}$	134	100.00		

The decomposition just cited does not depend upon the presence of alcohol; for cymene is likewise formed when cuminol or cuminic alcohol is treated with melted hydrate of potash, and especially when the potash is either not heated strongly enough to oxidise the cuminol at the first contact, or when individual particles of the fused salt are cooled down by too rapid addition of the cuminol.

It is possible that similar processes may determine the simultaneous formation of cymene and cuminol in the living plant; at all events

the assumption that a hydrocarbon is produced by the decomposition of an oxygenised constituent, is more strongly supported by analogy than that of a direct reduction or oxidation.

From the cymene obtained in the processes above described, the author prepared the hitherto unknown compound, *Dinitrocymene*. This body was obtained by cautiously dropping cymene into a mixture of 2 parts concentrated sulphuric and 1 part fuming nitric acid, heating the mixture to about 50° C., and leaving it to stand for a day or two. On subsequently diluting it with water, a brown substance separates, liquid at first, but becoming solid and crystalline after some time; this substance is a mixture of dinitrocymene and certain uncrystallisable products, formed in consequence of the action of the acids having been carried too far. From the solution in boiling alcohol, the non-crystallising bodies separate on cooling, whereas the dinitrocymene does not crystallise out till the liquid is evaporated. The crystals are colourless, beautifully iridescent, rhombic tables, which melt at 54° C., dissolve in ether and alcohol, but not in water, and separate from the saturated solution in the form of an oily liquid. When heated in the air, they detonate, and leave a very slowly combustible charcoal. The results of their analysis are as follows:—

	Calculated.		Found.	
20 C . .	120	53·57	52·13	53·39
12 H . .	12	5·36	5·28	6·04
2 NO ₄ . .	92	41·07		
<hr/>				
C ₂₀ { $\begin{smallmatrix} \text{H}_{12} \\ 2 \text{NO}_4 \end{smallmatrix}$ }	224	100·00		

On Benzoic Alcohol.*

by S. Cannizzaro.

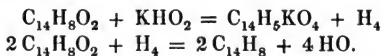
A NOTICE of the author's first observations on benzoic alcohol was given in vol. vii. p. 192 of this Journal. It was there stated that when the vapour is passed over red-hot spongy platinum, an oil is formed lighter than water, and having probably the composition C₄H₆. Subsequent observation, however, has shown that this is not the case, the oil in question, being a mixture of several products, among which benzene could be distinguished and separated; it contains also a solid body not yet examined.

Benzoic alcohol in contact with sulphuric acid, or when heated with chloride of zinc or anhydrous phosphoric acid, is converted into

* Ann. Ch. Pharm. xc. 252; xcii. 113.

a resinous substance, which is insoluble in water, alcohol, and ether, dissolves but sparingly in fuming sulphuric acid, and softens in boiling water (*vid. seq.*)

Benzoic alcohol, when treated with potash, yields benzoate of potash and a hydrocarbon (toluol, Deville's benzoene). Under the influence of reducing agents, therefore, the alcohol is converted into a hydrocarbon, which stands to it in the same relation as marsh-gas to wood-spirit:—



To obtain this hydrocarbon, the alcohol is distilled with a strong alcoholic solution of potash; as soon as all the alcohol has passed over, and the residue has become solid, the hydrocarbon begins to pass over mixed with undecomposed benzoic alcohol. To obtain the hydrocarbon pure, the liquid which has passed over is again distilled, the portion which goes over at 116° being collected apart; this distillate is mixed with strong sulphuric acid, which resinifies the benzoic alcohol, and the decanted liquid is washed with water and rectified over anhydrous phosphoric acid. The product thus obtained does not solidify in a freezing mixture; it boils at 114° ; has an agreeable odour like that of benzin. Its analysis gave 91.223 per cent. carbon and 8.738 hydrogen (mean), which agrees very nearly with the formula C_{14}H_8 , that formula requiring 91.305 C. and 8.695 H. The boiling point, 114° , corresponds with that which Gerhardt found for toluol; the odour is exactly the same.

Just as acetic ether obtained from common alcohol is polymeric with aldehyde, and probably isomeric with metaldehyde, so likewise is the benzoic acid ether of benzoic alcohol polymeric with the aldehyde of this alcohol, viz. bitter almond oil, and isomeric with benzoin. This ether is obtained by distilling equal equivalents of chloride of benzoyl and benzoic alcohol, or by distilling benzoic alcohol with Gerhardt's anhydrous benzoic acid. As the distillate cools, the ether crystallises out, surrounded with a yellow oil, which does not alter its composition to any great extent. It crystallises in snow-white needles, often in rhombohedrons; above 20°C . it melts to a colourless oil, which remains liquid for a day, and solidifies only when exposed to a freezing mixture. Its formula is $\text{C}_{28}\text{H}_{12}\text{O}_4$.

Fluoride of silicium has no action on benzoic alcohol. Fluoride of boron, on the contrary, attacks it vigorously, forming boracic acid, hydrofluat of boracic acid, and a resinous substance. After being washed, first with alkaline water, then with pure water, alcohol, and ether, dried at 170° , dissolved in sulphide of carbon or in chloroform, separated from the solvent by evaporation and fusion, it forms an amorphous, translucent, amber-coloured substance, which is insoluble in water, nearly insoluble in alcohol, dissolves very sparingly in

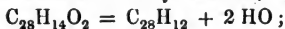
ether, but very readily in oil of turpentine, sulphide of carbon, and chloroform; becomes soft and melts when heated, and decomposes at a higher temperature, yielding both solid and fluid volatile products, and leaving a residue of charcoal. It gave by analysis 92·860 per cent. carbon, and 6·817 hydrogen, agreeing nearly with the formula $C_{14}H_6$; but its physical properties show that its true formula is a multiple of $C_{14}H_6$, probably $C_{28}H_{12}$, which would make it isomeric with stilbene.

Fused boracic acid acts on benzoic alcohol in two different ways. Between 100° and $120^\circ C.$, it converts the alcohol into the corresponding ether, $C_{28}H_{14}O_2$, and at a higher temperature into the resinous substance $C_{28}H_{12}$. This latter body is also formed by the action of anhydrous phosphoric acid.

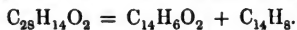
The ether corresponding to benzoic alcohol may be prepared as follows:—The alcohol is made into a paste with fused and pulverised boracic acid, and the mixture heated to 120° or 125° for several hours in a sealed tube immersed in an oil-bath. The mixture hardens and turns brown. It is treated with boiling water and with a solution of alkaline carbonate, till all the boracic acid is dissolved, and a greenish brown oil floats on the surface of the liquid. This oil is distilled; the portion which goes over below $300^\circ C.$ contains unaltered benzoic alcohol; but that which distils over between 300° and 315° contains the benzoic ether. In the retort there remains a quantity of the resinous hydrocarbon saturated with the ether, which cannot be separated from it without decomposition. Benzoic ether is a colourless oily liquid, which, when viewed in certain directions, exhibits a slight indigo-colour. It boils between 310° and 315° . It gives by analysis 84·5 per cent. carbon, and 7·3 hydrogen, the formula $C_{28}H_{14}O_2$ requiring 84·8 C and 7·1 H.

Benzoic ether treated with sulphuric or phosphoric acid, yields a resinous substance, probably identical with that which is obtained from the alcohol.

When heated in a sealed tube to a few degrees above 315° , the ether decomposes, becoming amber-coloured, and yielding a very small quantity of the resinous body, together with bitter-almond oil (which may be separated by bisulphite of soda), and a light oil, probably consisting of toluol. A small portion of the ether appears, therefore, to be resolved into water and the hydrocarbon, $C_{28}H_{12}$:



while the greater part is resolved into hydride of benzoyl and toluol:



On the Anilides of Pyrotartaric Acid.

By E. Arppe.

Pyrotartanil, $C_{22}H_{11}NO_4$ ($=C_{12}H_7N, C_{10}H_8O_8-4HO$).—When crystallised pyrotartaric acid is fused with aniline in the proportion of 2 eq. of the acid ($C_5H_4O_4$) to 1 eq. of aniline ($C_{12}H_7N$), and the mixture kept for about ten minutes at a temperature a few degrees above 100° , a brown viscid mass is obtained, which, when stirred with a glass rod, begins to crystallise, and assumes the form of a dirty-red solid mass, consisting of impure *Pyrotartanil*. This substance, after being twice heated with animal charcoal in a boiling aqueous solution, separates on cooling in the form of a perfectly white, tasteless, inodorous, crystalline powder, which under the microscope exhibits the appearance of delicate needles.

Pyrotartanil melts at $98^\circ C.$, and runs in boiling water like an oil, which, on cooling, solidifies in a crystalline fatty mass. It volatilises without decomposition; at $140^\circ C.$ it sublimes pretty quickly, giving off a vapour which has a faint odour, and adheres to cold bodies in the form of a very hard crystallisation. By boiling, during which the temperature may gradually rise to 300° , it is partially decomposed, the greater part, however, collecting in the neck of the retort, in the form of a tolerably pure and more or less distinctly crystalline sublimate of unaltered pyrotartanil. Hence very impure pyrotartanil may be conveniently purified by slow distillation.

Pyrotartanil dissolves but sparingly in water, even at a boiling heat. Alcohol dissolves it readily, and moreover, greatly assists the solvent power of boiling water, without hindering the subsequent separation in cooling; hence weak spirit is the best solvent to use when impure pyrotartanil is to be decolorised by animal charcoal. Pyrotartanil is also readily soluble in ether and in the ordinary acids. Alkalies dissolve it without alteration; but on heating the solution, the pyrotartanil is first converted into pyrotartanilic acid, and then resolved by the action of the fixed alkali into aniline and pyrotartaric acid. Very strong nitric acid converts it into pyrotartanonitril. The composition of pyrotartanil is as follows:—

	Calculated.	Found.
22 C . . 132	69.84	69.81
11 H . . 11	5.82	5.92
N . . 14	7.41	
4 O . . 32	16.93	
<hr/> C ₂₂ H ₁₁ NO ₄ <hr/>	<hr/> 189 <hr/>	<hr/> 100.00 <hr/>

2. *Pyrotartanilic acid*, $C_{22}H_{13}NO_6$ ($=C_{12}H_7N, C_{10}H_8O_8-2HO$).—When aniline is added by drops and with stirring to pyrotartaric

anhydride (the watery oil obtained by distilling pyrotartaric acid may be used for the purpose), the mass becomes very hot, and solidifies to a reddish crystalline magma of pyrotartanilic acid, which ultimately crumbles to pieces and becomes nearly dry; it may be purified by boiling with weak alcohol and animal charcoal in the manner described for the purification of pyrotartanil.

Pyrotartanilic acid separates on cooling from a boiling solution, in a bulky mass of shining crystalline needles, which, if the solution is not very concentrated, are arranged in stellate groups, and exhibit under the microscope the appearance of rectangular prisms, with perpendicular terminal faces. It bears a heat of 140° C. almost without loss; melts at 147° , giving off water, and being partially converted into the more easily fusible pyrotartanil; hence the acid, after one fusion, melts at 140° . It dissolves rather slowly in water, though in greater quantity than pyrotartanil; alcohol, however, dissolves it readily, and from the alcoholic solution it is precipitated in the crystalline form by water. With ether and with acids it behaves like pyrotartanil. It is decomposed by boiling with excess of potash. Neither pyrotartanil nor pyrotartanilic acid gives the characteristic reaction of aniline with solution of chloride of lime.

Pyrotartanilic acid is a very stable though rather weak acid. It reddens litmus paper, expels carbonic acid from carbonates, forms several crystallisable salts, but is precipitated in the crystalline form from its solutions by other acids, even by acetic acid. The pyrotartanilates of the alkalis and earths are easily soluble; those of the heavy metallic oxides, sparingly soluble. In a solution of the neutral ammonia-salt, no precipitate is formed by chloride of barium or calcium, or by baryta or lime-water; sulphate of zinc produces a turbidity after a while; sulphate of copper forms a bluish-green, and sesquichloride of iron a yellowish-red precipitate.

The analysis of the acid dried at 140° and at 100° gave the following results:—

			Found.	
			At 140°.	At 100°.
22 C . . .	132	Calculated. 63.77	63.84	63.60
13 H . . .	13	6.28	6.54	6.32
N . . .	14	6.76		
6 O . . .	48	23.19		
<hr/> C ₂₂ H ₁₃ NO ₆		<hr/> 207		
		100.00		

Pyrotartanilate of ammonia dries up to a radiated crystalline mass, easily gives up its ammonia, and is decomposed by water with the aid of heat; in the cold, it is readily dissolved if perfectly neutral. It is likewise formed by boiling pyrotartanil with ammonia. The *potash-*

salt resembles the ammonia-salt, and dissolves readily in water. The *soda-salt* dries up to a confused crystalline mass. The *baryta-salt* becomes granular and crystalline when thoroughly dried. The *lime-salt* forms needles having a dull silky lustre. The *lead-salt* PbO , $\text{C}_{22}\text{H}_{12}\text{NO}_5$ —, forms a white precipitate, which becomes pasty by boiling, but when left to itself assumes a granular crystalline character, and melts at a higher temperature; it dissolves in acetate of lead and in boiling water. The *silver-salt*, AgO , $\text{C}_{22}\text{H}_{12}\text{NO}_5$, is a white pulverulent body, which dissolves in water, and separates again on evaporation in small round crystalline nodules. It contains 34.36 per cent. silver.

3. *Pyrotartonitranyl*, $\text{C}_{22}(\text{H}_{10}\text{NO}_4)\text{NO}_4$.—This compound, in which 1 eq. of the hydrogen in pyrotartanyl is replaced by 1 eq. of hyponitric acid, is produced with the greatest facility by dissolving pyrotartanyl in the very strong nitric acid obtained by distillation with sulphuric acid. The solution assumes a red colour for a while, but afterwards becomes yellow, and, on addition of water, deposits a gradually solidifying oil, which, after being resolved in boiling alcohol, decolorised by animal charcoal, and filtered, yields pure pyrotartonitranyl in crystalline needles arranged in spherical groups.

Pyrotartonitranyl melts at 155° , and solidifies in the crystalline state at 153° ; sublimes without decomposition when carefully heated, dissolves in alcohol and ether; but is nearly insoluble in water. By boiling with ammonia, it is converted into an acid, which is likewise produced by the action of the fixed alkalies, but is readily transformed by the latter into a yellow crystalline substance.

Pyrotartonitranyl yields the following results by analysis:—

		Calculated.	Found.
22 C	. . 132	56.41	56.35
10 H	. . 10	4.27	4.34
2 N	. . 28	11.97	
8 O	. . 64	27.35	
<hr/>		<hr/>	
$\text{C}_{22}\text{H}_{10}\text{N}_2\text{O}_8$	234	100.00	

4. *Pyrotartonitrilic acid*, $\text{C}_{22}(\text{H}_{10}\text{NO}_4)\text{NO}_6$.—When pyrotartonitranyl is added to a somewhat dilute solution of carbonate of soda, it is quickly dissolved, while the solution assumes a yellow colour, and a slight evolution of carbonic acid becomes perceptible. If the yellow solution be cooled, yellow crystals of nitranyl (vid. inf.) separate out from it.

The clear yellow solution consists chiefly of pyrotartonitrilic acid, which, on the addition of nitric acid in excess, is precipitated in yellow flakes. It is decolorised partly by animal charcoal, partly by recrystallisation, but is not easily obtained in a state of perfect purity.

This acid dissolves very sparingly in water, even at a boiling heat, but readily in alcohol and ether; from a saturated solution, it separates in a distinctly crystalline form, and when examined by the microscope appears to consist of rhombic tables having angles of 60° and 120° . It is so weak an acid that it is scarcely able to expel carbonic acid. After drying over sulphuric acid, it gave the following results by analysis:—

		Calculated.	Found.
22 C	. . 132	52.38	52.46
12 H	. . 12	4.76	4.89
2 N	. . 28	11.11	
10 O	. . 80	31.75	
<hr/>		<hr/>	
$C_{22}H_{12}N_2O_{10}$	252	100.00	

The salts of this acid are very unstable and uncrystallisable. The *potash-salt* scarcely exists in the solid state, the solution of the acid in potash quickly decomposing and assuming an intense yellow colour. The *ammonia-salt* dries up to a syrup. The *silver-salt* precipitates in white flakes, and is found by analysis to contain 30.13 per cent. silver, the formula requiring 30.10 per cent.

On Nitraniline and Paranitraniline.*

By E. Arppe.

THE yellow body produced by the action of alkalis on pyrotartaronitrilic acid is identical in composition with the nitraniline which Hofmann and Muspratt obtained from dinitrobenzol, $C_{12}H_4N_2O_8$.† The two bodies, however, differ remarkably in many of their properties; and as the substance produced by Arppe is produced directly from an aniline-compound, he proposes to assign to it the name of *Nitraniline*, and to designate as *Paranitraniline* the isomeric compound produced from dinitrobenzol.

1. Nitraniline.—This base is most readily obtained by boiling pyrotartaronitril or pyrotartaronitrilic acid in a solution of carbonate of soda mixed with a little caustic soda; the decomposition is then completed in a quarter of an hour, and the solution on cooling deposits nitraniline in yellow laminæ, which may be purified by recrystallisation.

From a slowly cooled aqueous solution, nitraniline separates in long needles; but if the cooling be accelerated, small tabular or needle-shaped crystals are obtained, having angles of 69° and 111° , but with

* Ann. Ch. Pharm. xc. 147; xciii. 357.

† Ibid. lviii. 215.

the smaller angle so much truncated as to convert the crystal into a six-sided table with angles of 111° and 138° . An alcoholic solution, on the other hand, yields unaltered rhombic tables as well as these six-sided crystals; from ether, the compound separates, partly in tables, partly in capillary needles; from carbonate of soda, in tables of 55° and 125° ; by sublimation it is obtained partly in needles, partly in irregular laminæ.

Nitraniline melts (according to the latest determination) at 141° , volatilises at about the same temperature, and sublimes very beautifully when carefully heated between two watch-glasses. It dissolves readily in alcohol and ether, but requires 45 parts of boiling water, and no less than 1250 parts of water at 18.5° to dissolve it completely. Its analysis gave 52.03 per cent. carbon, and 4.44 hydrogen, agreeing very nearly with the formula $C_{12}H_6N_2O_4$, which requires 52.17 per cent. carbon, and 4.35 hydrogen.

Hydrochlorate of Nitraniline, $C_{12}H_6N_2O_4 \cdot HCl$. — Nitraniline forms with boiling hydrochloric acid a yellow, or if the acid is in great excess, a colourless solution, which on cooling yields tolerably large colourless tabular crystals, the simplest forms of which are four-sided tables of 95° and 85° (*a*), or of 65° and 115° (*b*); by the combinations of these, whereby the acute angles of (*a*) are truncated by (*b*), six-sided tables are produced, and by truncation of all the angles of (*a*), eight-sided tables.

The salt is easily decomposed, both when heated, whereby it loses part of its acid and turns yellow, and also by the action of water, by which the base is almost completely precipitated; alkalies precipitate the nitraniline in the crystalline form, but it is redissolved when heated with an excess of the precipitant. The hydrochlorate gives by analysis 20.20 per cent. chlorine, the formula requiring 20.34.

Platinum-salts. — Hydrochlorate of nitraniline forms two double salts with bichloride of platinum; but that which has the normal composition, $C_{12}H_6N_2O_4 \cdot HCl \cdot PtCl_2$, is difficult to obtain.

1. The best mode of preparing this normal salt is to mix a concentrated aqueous or alcoholic solution of bichloride of platinum with a warm concentrated solution of nitraniline in hydrochloric acid, collect the resulting precipitate in an empty glass funnel, leave the mother-liquor to drain off, and wash the precipitate, first with an alcoholic solution of nitraniline, and afterwards with ether; or to mix the concentrated alcoholic solutions of the two chlorides, wash the precipitate with a small quantity of water, and remove the mother-liquor as completely as possible by pressure. This salt when dry has a yellow colour; it crystallises with the greatest facility from a concentrated alcoholic solution, separating almost instantly in capillary needles, arranged in stellate groups; it may be heated considerably above 100° without decomposition, but burns away with slight detonation at a higher temperature. The aqueous solution is decomposed by evapo-

ration; the solution in alcohol is more permanent. The salt gave by analysis 28.22 per cent. platinum; the formula requires 28.72 per cent. ($\text{Pt}=98.5$). As this salt is much more soluble in alcohol than in water, an abundant crystalline precipitate is obtained on adding water to a concentrated alcoholic solution. This precipitate dried at 100° contained 28.45 per cent. platinum, and consisted, therefore, of the unaltered double salt.

2. If the double salt obtained as above be washed with a mixture of alcohol and ether, it is decomposed, and there remains a less soluble yellow compound, $\text{C}_{12}\text{H}_6\text{N}_2\text{O}_4 \cdot \text{HCl} + 2\text{PtCl}_2$, in which the quantity of platinum given by analysis is 38.16, the formula requiring 38.36. This salt is partially dissolved, with red colour, by alkalies, the rest being left in the form of a brick-red powder, which dissolves with red colour in water and alcohol. From the aqueous solution crystals were once obtained having the form of small red regular octohedrons; but, from want of material, they were not further examined.

Sulphate of Nitraniline.—A solution of nitraniline in dilute sulphuric acid yields by gentle evaporation large shining laminae, the smaller crystals of which exhibit under the microscope the form of square tables. The salt has a strongly acid taste, is decomposed by water, but remains unaltered in the acid. The biacid salt, $\text{C}_{12}\text{H}_6\text{N}_2\text{O}_4 + 2(\text{HO.SO}_3)$ contains by calculation 33.90 per cent. sulphuric acid; analysis gave 34.41 per cent.

Nitrate of Nitraniline.—The base dissolves very easily in warm nitric acid, and the salt crystallises in shining needles several lines long and perpendicularly truncated: it is decomposed by water.

The *oxalate* crystallises in delicate needles and laminae; it is an acid salt sparingly soluble in water, and forming a yellow solution.

The *tartrate* forms a yellow solution which deposits yellow needles; potash does not precipitate, but dissolves it with red colour.

When a recently prepared solution of tannic acid is added to a solution of hydrochlorate of nitraniline, and afterwards a little potash-solution poured in, a copious flocculent or almost gummy precipitate is formed, which is decomposed by an excess of potash, part of the base separating in the crystalline form.

2. *Paranitraniline.*—This substance was prepared, according to Hofmann and Muspratt's directions, by the action of sulphuretted hydrogen on an alcoholic solution of dinitrobenzol saturated with ammoniacal gas. After treating the solution with animal charcoal, the base was obtained in very beautiful yellow, highly lustrous, long, flattened, needle-shaped crystals. These crystals gave by analysis 52.01 per cent. carbon, and 4.37 hydrogen, the formula $\text{C}_{12}\text{H}_6\text{N}_2\text{O}_4$ requiring 52.17 C and 4.35 H.

Paranitraniline melts at 108° (Hofmann and Muspratt fix the melting point at 110°) and volatilises at about the same temperature,

forming a sublimate of yellow shining laminæ, which by micrometrical examination were found to consist of rhombic tables of 51° and 129° , having one of their acute angles either perpendicularly truncated or bevelled with two faces, but the two obtuse angles either obliquely truncated or unaltered. They often unite in macles with a deep re-entering angle, this macle-formation being likewise indicated by a feathery striation of the lamellæ, passing in two different directions. The crystals separated from solutions exhibit a similar want of symmetry. The laminæ which separate from the aqueous solution are perpendicularly truncated at one end and bevelled at the other, with two faces inclined at 98° to one another, and 131° to the adjacent faces. From the alcoholic solution the base separates by spontaneous evaporation, partly in small wedged-shaped four-sided laminæ, two of whose faces are likewise inclined to one another at an angle of 98° , while the other two form a very acute angle,—partly in somewhat large crystals with re-entering obtuse angles.

Paranitraniline dissolves sparingly in water, requiring 600 times its weight of water at 18.5° to dissolve it; in boiling water it dissolves more readily, likewise in alcohol and ether.

With *hydrochloric acid* it forms a colourless solution, from which elongated rhombic tables of 120° and 60° separate. This salt dissolves readily in hydrochloric acid, is not altered by exposure to the air, but is decomposed by water in such a manner that the greater part of the base separates out,—a statement contradictory to that of Hofmann and Muspratt, who found their hydrochlorate of nitraniline to dissolve in water with extraordinary facility.

Sulphate of Paranitraniline forms shining microscopic crystals, consisting of rhombic tables, which have but little taste, and form a perfectly colourless solution in water. Potash and ammonia precipitate the base in the crystalline form.

Nitrate of Paranitraniline is a crystalline powder sparingly soluble in the acid, easily in water; hence the nitric acid poured on the base forms a white crystalline powder, which disappears on the addition of water. The author has not been able to confirm the statement of Hofmann and Muspratt, that paranitraniline is decomposed with violence by nitric acid.

Tartrate of Paranitraniline forms a yellow solution from which yellow rectangular tables separate; potash added to the solution throws down the base in the form of a yellow crystalline precipitate insoluble in excess of the reagent.

Tannic acid acts with paranitraniline in the same manner as with nitraniline.

From the preceding description of nitraniline and paranitraniline, it is clear that these two bases are essentially distinct and cannot be easily confounded. They are more especially distinguished by their

melting points, their crystalline forms, and their relations to various solvents; moreover, their sulphates, nitrates, and tartrates, exhibit essential differences. But they also present other points of distinction more easily recognisable. Paranitraniline has a sweet burning taste, whereas nitraniline is nearly tasteless. Paranitraniline has a deeper yellow colour than nitraniline; its saturated solution is nearly orange-yellow, and becomes paler on cooling; the colour of nitraniline, as well as that of its solution, is always light yellow. Paranitraniline has a strong lustre; the crystalline needles which it forms are flexible or elastic, and therefore difficult to pulverise; nitraniline has a fainter lustre, and its crystalline needles are brittle, and easily rendered electrical by friction.

On the Anilides of Tartaric Acid.*

By E. Arppe.

TARTARIC ACID forms with aniline a crystalline salt, which, if tartaric acid be regarded as monobasic, exhibits the composition of a bitartrate. This salt begins to decompose at temperatures a little above 100° ; if it be kept for some time between 130° and 140° , it turns brown, giving off vapours of water and aniline, and, at the same time, a new crystalline body is formed, which covers and penetrates the dark mass. At 150° , partial fusion takes place, after which the addition of solution of chloride of lime no longer indicates the presence of unaltered aniline.

The resulting preparation is thoroughly boiled with water, whereby *Tartanil* is extracted, which substance must then be purified by repeated crystallisation and treatment with animal charcoal.

The brown mass which remains undissolved by the water is boiled with strong alcohol, which dissolves it completely, and on cooling yields delicate crystals, which may be decolorised by the ordinary methods: these crystals consist of *Tartanilide*.

1. *Tartanilide*, $C_{32}H_{16}N_2O_8$ ($= 2C_{12}H_7N \cdot C_8H_6O_{13} - 4HO$), is insoluble in water, sparingly soluble in ether, and is not taken up in large quantity even by boiling alcohol. From the hot saturated alcoholic solution, it is deposited on cooling in fine colourless needles, which, when collected on a filter and pressed, aggregate together in nacreous laminated masses, retaining their continuity even after drying. It may be heated to 250° without visible decomposition, but is decomposed when fused; sublimes somewhat above its melting-point; and when carefully heated between two watch glasses, yields

* Ann. Ch. Pharm. xciii. 352.

a sublimate of shining iridescent laminæ, which, however, not being very volatile, remain adhering to the unfused portion. At a higher temperature, a dull crystalline or mealy sublimate is obtained.

Tartanilide is a very stable substance; it may be boiled in alkaline solutions without alteration; hot hydrochloric acid dissolves it with difficulty, nitric acid with partial decomposition; sulphuric acid is the only acid which dissolves it readily.

		Calculated.	Found.
32 C	. . . 192	64.000	63.61
16 H	. . . 16	5.334	5.40
2 N	. . . 28	9.334	
8 O	. . . 64	21.332	
<hr/>		<hr/>	
$C_{32}H_{16}N_2O_8$	300	100.000	

2. *Tartanil*, $C_{20}H_9NO_8$ ($=C_{12}H_7N \cdot C_8H_6O_{12}-4 HO$), dissolves very readily in water and alcohol, and separates from hot concentrated solutions, either as a dull white fine-grained powder, or in laminæ having a pearly lustre. Slow cooling and perfect purity in the preparation favour the production of the crystalline modification; and, on the other hand, sudden cooling and the presence of a small quantity of tartaric acid appear to give rise to the granular variety.

Tartanil bears a heat of more than $200^\circ C$. without decomposition; the granular variety, however, passes at that temperature into the crystalline, but without any change of chemical composition; the sublimate thereby obtained forms an extremely delicate, woolly crystallisation of unaltered tartanil. At 230° , fusion and decomposition take place.

Tartanil has no taste, but reddens litmus perceptibly even when perfectly pure. It dissolves but slowly in ether, but is readily taken up by other solvents.

		Calculated.	Found.
20 C	. . . 120	57.97	57.71
9 H	. . . 9	4.35	4.38
N	. . . 14	6.76	
8 O	. . . 64	30.92	
<hr/>		<hr/>	
$C_{20}H_9NO_8$	207	100.00	

3. *Tartanilic Acid*, $C_{20}H_{11}NO_{10}$, is obtained by boiling tartanil for about a quarter of an hour with a solution of ammonia, evaporating the excess of ammonia at a gentle heat, adding baryta-water in excess to the solution, washing the copious precipitate which is thereby formed, and decomposing it with sulphuric acid. From the filtered solution, the tartanilic acid separates, partly in light red nodular crystalline masses, partly in shining laminæ. After purifi-

cation with animal charcoal, this acid forms colourless laminæ having a strong lustre. It melts at 180°C. , and is at the same time partially decomposed, with loss of water. It dissolves without difficulty in water and alcohol, but is much less soluble in ether.

Tartanilate of Ammonia, after evaporation over sulphuric acid, forms a very efflorescent, easily soluble crystalline mass. A solution of this salt gives no precipitate with lime-water, even after addition of ammonia; but if potash be added, a turbidity is produced, which increases on boiling, and passes into a copious bulky precipitate. Chloride of calcium and chloride of barium form no precipitates, not even on addition of excess of ammonia. Baryta-water forms a copious precipitate, soluble in sal-ammoniac, sesquichloride of iron, or yellow precipitate.

Tartanilate of Baryta is soluble to a considerable extent in boiling water, and separates on evaporation in shining, irregular, crystalline spangles. It yields by analysis 26.10 per cent. baryta, corresponding to the formula $\text{BaO} \cdot \text{C}_{20}\text{H}_{10}\text{NO}_9$, which requires 26.15 per cent. baryta ($\text{Ba} = 68.5$).

Tartanilate of Silver forms a white somewhat soluble powder, containing 32.66 per cent. silver. The formula $\text{AgO} \cdot \text{C}_{20}\text{H}_{10}\text{NO}_9$ requires 32.55 per cent.

4. *On the action of Nitric Acid upon Tartanil and Tartanilide.*—Nitric acid, rectified over sulphuric acid, acts strongly on these bodies. On mixing them with the acid, considerable heat is evolved, accompanied with formation of picric acid. If the rise of temperature be prevented by immersing the vessel containing the nitric acid in snow and adding the anilides by small quantities, a solution is obtained, from which water throws down a yellowish body quite insoluble in water, very sparingly soluble in alcohol, and presenting under the microscope the appearance of a crystalline powder. When this nitro-compound is boiled with carbonate of soda, part of it is dissolved, but the solution does not yield crystals. The greater portion remains undissolved, and appears to contain picric acid.

As these experiments did not lead to the preparation of nitraniline, the author discontinued them, and did not examine any further into the chemical relations of tartonitraniline.

The *Anilides of Racemic Acid* appear to be identical with those of tartaric acid; for the author has obtained from racemate of aniline compounds which do not differ from tartanil and tartanilide, at least in their external characters.

On Salicylic Acid.***By R. Piria.**

THIS acid, usually regarded as monobasic, nevertheless exhibits the singular anomaly of forming acid ethers, analogous rather to the acid ethers of polybasic acids than to neutral ethers. In the course of investigations relating to this matter, the author has succeeded in discovering the cause of this anomaly, or, rather, he has found that it does not actually exist. The truth is, that salicylic acid, which has hitherto been regarded as monobasic, is really bibasic, and in a very marked degree,—forming, with the utmost facility, salts with two equivalents of base. The salts with 1 eq. of base, which are those already known, may for distinction be denominated *acid salicylates*; and the newly-discovered salts with 2 eq. of base, *neutral salicylates*.

The neutral *baryta-salt* is prepared by adding a concentrated solution of hydrate of baryta to a concentrated boiling solution of the acid salicylate; as the neutral salt is much less soluble than the acid salt, it separates out immediately in small white crystalline laminæ, which may be purified by recrystallisation from boiling water. This salt has a very decided alkaline reaction; in the state of aqueous solution, it is decomposed by carbonic acid, salicylate of baryta being formed, and half the baryta precipitated as carbonate. The composition of the neutral salt is, $C_{14}H_4Ba_2O_6 + 4Aq.$; at 100° it gives off 4 eq. water, and becomes anhydrous.

The neutral *lime-salt* is prepared with equal facility. When a solution of lime in sugar-water is added to a solution of acid salicylate of lime, the neutral salt separates immediately as a nearly insoluble, crystalline, sandy precipitate, which has an alkaline reaction, and is decomposed by carbonic acid like the baryta-salt. The composition of the neutral lime-salt is $C_{14}H_4Ca_2O_6 + 2Aq.$

The neutral *lead-salt* is anhydrous, and forms a heavy white crystalline powder, having the composition $C_{14}H_4Pb_2O_6$. It is easily obtained by adding tribasic acetate of lead to a saturated boiling solution of the acid salicylate. If this acid lead-salt be decomposed by ammonia in slight excess, and the resulting mixture boiled, a pentabasic salicylate, $C_{14}H_4Pb_2O_6 + 3PbO$, falls down as a light, insoluble, white powder, consisting of microscopic laminæ, which have a pearly lustre.

The *cupric salts* of salicylic acid had not been previously examined. Piria has prepared the acid salicylate by decomposing the acid salicylate of baryta with a solution of cupric sulphate; it crystallises in long bluish-green needles, having the composition $C_{14}H_5CuO_6 + 4Aq.$ It gives off its water of crystallisation considerably below 100° . This salt exhibits remarkable properties. When heated in a small quantity of water, not sufficient to dissolve it completely, it melts below 100° ,

* Ann. Ch. Pharm. xciii. 262.

and is converted into the neutral salt, which remains undissolved, and free salicylic acid, which dissolves in the water. Ether decomposes it in a similar manner at ordinary temperatures.

The neutral copper-salt obtained in the manner above described by the decomposition of the acid salt, is a light, nearly insoluble powder, of yellowish-green colour: its formula is $C_{14}H_4Cu_2O_6 + 2 Aq.$

Piria has likewise obtained two neutral salicylates, in which the two equivalents of base are formed by different metals, viz., a potassio-cupric salicylate, $C_{14}H_4KCuO_6 + 4 Aq.$, which crystallises in beautiful emerald-green laminæ, and baryto-cupric salicylate, which forms a crystalline powder containing $C_{14}H_4BaCuO_6 + 4 Aq.$

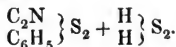
On some Compounds of Hydrosulphate of Mustard-oil.*

By H. WILL.

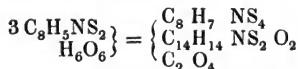
In a memoir on the essential oil of black mustard,† the author has demonstrated the existence of a compound of that oil with sulphuretted hydrogen, having the formula $C_6H_5NS_2 \cdot H_2S_2$. Gmelin‡ denominates this compound *Sulphosinapic acid*; Gerhardt§ regards it as sulphocarbamic acid in which 1 eq. hydrogen is replaced by allyl, C_6H_5 ; thus:—



According to Will's formula, it is sulphocyanide of allyl combined with sulphuretted hydrogen:—



Will formerly obtained the compound by the action of an alcoholic solution of potash upon oil of mustard, it being then produced, together with carbonic acid and an oily body, $C_{14}H_{14}N_2S_2O_2$, in the manner represented by the equation—



On separating the oily body, neutralising with acetic acid, diluting the

* Ann. Ch. Pharm. xcii. 59.

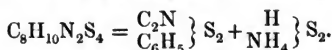
† Ibid. lii. 30.

‡ Handb. d. Chem. 4. Aufl. v. 207.

§ Traité de Chimie Organique, ii. 203.

solution with a large quantity of water, and adding acetate of lead, a lemon-yellow, very unstable lead-salt is thrown down, whose analysis leads to the formula $C_8H_5NS_2 + \frac{HS}{PbS}$. From the author's more recent experiments, it appears that the whole of the mustard-oil may be readily converted into the sulphur-acid by treating it directly with alcoholic solutions of metallic hydrosulphates. In this manner the following compounds have been obtained, the analyses of which confirm the composition of the acid previously deduced from the lead-salt :—

Oil of Mustard with Hydrosulphate of Ammonium :

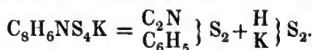


When oil of mustard is dropped into a saturated and colourless solution of hydrosulphate of ammonium in strong alcohol, its odour is instantly destroyed, the liquid becomes strongly heated, and in a few seconds solidifies to a crystalline magma composed of colourless needles of the double salt.

				Calculation.	Experiment; dried <i>in vacuo</i> .	
8 C	.	.	48	32.00	31.70	31.36
10 H	.	.	10	6.66	6.90	6.77
2 N	.	.	28	18.67	17.40	—
4 S	.	.	64	42.67	43.03	43.30
<hr/>				<hr/>	<hr/>	<hr/>
150				100.00	99.03	

This salt is not very stable, but, like the following compounds, decomposes spontaneously by keeping.

Oil of Mustard with Hydrosulphate of Potassium :



An alcoholic or aqueous solution of hydrosulphate of potassium, to which oil of mustard has been added as long as the odour of the latter disappears, yields by slow evaporation *in vacuo* (provided the quantity of salt present is not too small) large rhombic tables, often an inch in diameter; by quicker evaporation, needle-shaped crystals are formed. These crystals, while immersed in the liquid, are transparent and colourless, but on exposure to the air become opaque and yellow, losing their form and becoming partially insoluble in water, which then leaves a sulphur-yellow mass. The aqueous solution of the

recently-prepared salt may be heated without evolving the odour of mustard-oil; if it be heated and then mixed with nitrate of silver, sulphide of silver is precipitated, and the odour of mustard-oil becomes immediately perceptible. The dry compound likewise gives off mustard-oil when heated :—

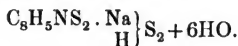
		Calculation.	Experiment.
8 C	. . 48·0	28·04	—
6 H	. . 6·0	3·50	—
N	. . 14·0	8·18	—
4 S	. . 64·0	37·38	38·09
K	. . 39·2	22·90	22·50
	<hr/> 171·2	<hr/> 100·00	

Oil of Mustard with Sulphide of Potassium.—*a.* $C_8H_5NS_2 + 2KS$.—An alcoholic solution of monosulphide of potassium mixed with oil of mustard, the former being in slight excess, deposits by gentle evaporation a white granular salt, which, when heated, gives off oil of mustard, without changing its colour. It gave by analysis 39·2 per cent. of potassium; the formula requires 37·4.

b. $C_8H_5NS_2 + KS$.—The mother-liquor from which the preceding salt has separated, yields, when left to stand over sulphuric acid *in vacuo*, needle-shaped crystals having a scarcely perceptible tinge of yellow: they behave like the preceding salt, but contain less potassium. Analysis gave 25·5 and 25·0 per cent. potassium, the formula *b* requiring 25·4.

It appears, then, that oil of mustard forms crystallisable salts, not only with the hydrosulphates, but also with the monosulphides of metals, and that the combination with the latter takes place in more than one proportion.

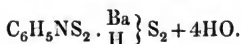
Oil of Mustard with Hydrosulphate of Sodium :



This compound is readily obtained by mixing a warm alcoholic solution of hydrosulphate of sodium with oil of mustard till the odour of the latter is no longer destroyed. It separates in nacreous laminæ which are greasy to the touch, and, when heated, first melt, and then give off a large quantity of mustard-oil. The salt contains water of crystallisation, and, like the preceding, cannot be preserved without decomposition.

		Calculation.	Experiment.	
8 C .	48·0	23·90	23·70	—
12 H .	12·0	5·73	5·93	—
N .	14·0	—	—	—
4 S .	64·0	—	—	—
6 O .	48·0	—	—	—
Na .	23·1	11·10	11·00	11·4
<hr/>				
		209·1		

Oil of Mustard with Hydrosulphate of Barium :



This salt is produced by adding oil of mustard to a solution of sulphide of barium supersaturated with sulphuretted hydrogen and mixed with a small quantity of alcohol, or by passing sulphuretted hydrogen gas through water mixed with alcohol, in which hydrate of baryta and oil of mustard are suspended; it is likewise deposited from the mother-liquor of the following less soluble salt containing monosulphide of barium. The more soluble salt forms crystalline laminæ, resembling those of the sodium-salt:—

		Calculation.	Experiment.	
8 C .	48·0	20·20	—	19·90
10 H .	10·0	4·23	—	4·60
N .	14·0	—	—	—
4 S .	64·0	—	—	26·5
4 O .	32·0	27·05	—	—
Ba .	68·6	29·00	30·4	30·44
<hr/>				
		236·6		

Oil of Mustard with Sulphide of Barium: $\text{C}_6\text{H}_5\text{NS}_2 \cdot 2\text{BaS} + 2\text{HO}$.
—When oil of mustard is gradually added to a yellow heated solution of sulphide of barium—such as is obtained by treating crude sulphide of barium with water—till the odour remains permanent, and the liquid filtered, the filtrate yields, on cooling, colourless or slightly yellowish laminæ, which crumble to a white powder on exposure to the air. This compound is also precipitated by alcohol. The salt smells of oil of mustard, does not melt when heated, but burns away with a glimmering light at a higher temperature. Two analyses made with the salt dried by repeated pressure between paper

gave 49.1 and 47.3 per cent. barium; the above formula requires 47.94.

This compound appears to be capable of crystallising with a different amount of water, inasmuch as a salt obtained in another preparation gave only 41.6 per cent. barium, which corresponds with the formula $C_8H_5NS_2 \cdot 2BaS + 6HO$ (calculated quantity of Ba = 42.6).

Oil of Mustard with Hydrosulphate of Calcium.—When milk of lime is mixed with oil of mustard, and a little alcohol added to dissolve the latter, the mustard odour disappears entirely on passing sulphuretted hydrogen through the liquid to supersaturation. A clear solution is then obtained, which, when evaporated over the water-bath, yields the calcium compound in the form of a slightly yellow transparent jelly. When perfectly dried, it falls to pieces, and gives off abundance of oil of mustard.

On Phillyrin.*

By C. Bertagnini.

THIS substance is obtained by treating the decoction of *Phillyrea* bark with lime or oxide of lead, and evaporating the liquid to a certain point, the phillyrin then separating after a while in the crystalline state.

Pure phillyrin is nearly tasteless; it dissolves very sparingly in cold water, with tolerable facility in hot water, readily in alcohol, but not in ether. Its solutions are not precipitated by those of metallic salts. Ammonia and the fixed alkalies have no action upon phillyrin, but mineral acids readily decompose it. When phillyrin is boiled with dilute hydrochloric acid, a resinous substance is produced, which separates in drops, and a liquid, which, when treated with Trommer's test-liquid, produces an abundant separation of cuprous oxide. Now as phillyrin and the resinous substance separated from it do not act on this test-liquid, it appeared probable that phillyrin is a substance of more complex constitution,—like amygdalin, salicin, &c.,—and capable, like these bodies, of yielding sugar as one of its products of decomposition.

When phillyrin is heated with a proper quantity of dilute hydrochloric acid, till the separation of resinous matter has ceased, the liquid neutralised with carbonate of lead, the filtrate evaporated, the residue exhausted with alcohol, and the alcoholic solution evaporated over the water-bath, a sweet syrup is obtained, which in a few weeks solidifies into a warty crystalline mass, exhibiting all the characters of grape-sugar.

* Ann. Ch. Pharm. xcii. 109.

An attempt was also made to decompose phillyrin with synaptase, but that substance does not act upon it.

To ensure that the substance combined with sugar in phillyrin is not separated by the hydrochloric acid in an altered state,—as is the case in the decomposition of salicin,—the phillyrin was subjected to the lactic acid fermentation, whereby it yielded, on the one hand, the usual products of the lactic acid fermentation of sugar, and on the other, the substance abovementioned, which may in this manner be readily obtained in the pure state. This substance, which may be called *Phillygenin*, is not sensibly altered by acids, and is perfectly identical with the resinous body which is produced, though not quite pure, by the action of hydrochloric acid on phillyrin. Pure phillygenin crystallises readily, and forms a perfectly white mass, having a pearly lustre. It is insoluble in cold water, very sparingly soluble in boiling water, but dissolves readily in alcohol and ether. Strong sulphuric acid colours it red.

The analyses of phillyrin, and of the several products derived from it, lead to the formula $C_{54}H_{34}O_{22} + 3 Aq.$

Calculated.		Found.			
Carbon	57.75	57.88	57.66	57.72	57.82
Hydrogen	6.63	6.63	6.72	6.82	6.73
Oxygen	35.62	35.49	35.62	35.46	35.45
	100.00	100.00	100.00	100.00	100.00

The 3 equivs. of water of crystallisation are given off between 50° and $60^{\circ} C.$, and at 100° the substance is perfectly anhydrous. The loss of weight which phillyrin sustains in drying is 4.7 per cent. ; by calculation it should be 4.8. The formula of anhydrous phillyrin is, therefore, $C_{54}H_{34}O_{22}$.

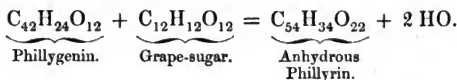
Phillygenin gave by analysis numbers corresponding with the formula $C_{42}H_{24}O_{12}$, as shown by the following table:—

Calculated.		Found.	
Carbon	67.74	67.83	67.60
Hydrogen	6.45	6.69	6.66
Oxygen	25.81	25.48	25.74
	100.00	100.00	100.00

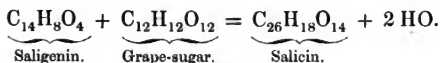
Phillygenin does not diminish perceptibly in weight when subjected to further drying; hence the formula just given must be regarded as that of anhydrous phillygenin.

Since phillyrin yields by decomposition nothing but grape-sugar and phillygenin, we are led to suppose that its constitution cor-

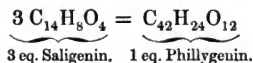
responds exactly with that of salicin, and that it is formed by the union of two groups of atoms with elimination of 2 eq. water, as shown by the following equation :—



This equation is precisely similar to that which expresses the constitution of salicin :—



On comparing the formulæ of phillygenin and saligenin, we discover a remarkable relation between them. Phillygenin is, in fact, polymeric with saligenin, its formula being exactly treble that of the latter :—



Phillyrin is converted by the action of chlorine into chloruretted or bromuretted derivatives, which crystallise in needles, and are less soluble than phillyrin. Their constitution is similar to that of phillyrin, and they are decomposed by the same reagents in a corresponding manner. Thus, for example, bromophillyrin, under the influence of acids or of the lactic-acid fermentation, yields grape-sugar or its decomposition-products, and bromophillygenin, which crystallises in shining needles.

Nitric acid acts differently on phillyrin according to its temperature and degree of concentration. With a dilute acid in the cold, a mass of yellow silky crystals is obtained. With strong acid, there is formed another product, which separates in crystalline grains. Lastly, if strong acid be used at a boiling heat, carbonic acid and nitrous fumes are evolved, and the liquid is found to contain oxalic acid, together with a product which crystallises in shining laminae.

On Mangostin.***By W. Schmid.**

THIS name is given to a yellow crystalline substance obtained from the rind of the fruit of the Mangosteen (*Garcinia mangostana*; Order, *Guttiferæ*), which is cultivated in the East Indian Islands. This fruit is one of the most delicious of tropical productions, and its rind is said to be very efficacious in the treatment of fevers, equalling, if not exceeding, that of cinchona-bark, especially when used in the fresh state.

To extract the active principle of this rind, a quantity of old dry rinds, which were of a brown-red colour, thick, spongy, of astringent taste, and lined in the interior with a yellow semi-crystalline substance, were finely pulverised, and repeatedly boiled with water. The aqueous solution consisted chiefly of tannin, which blackened iron-salts. The residue was then treated with hot alcohol, which completely dissolved the yellow crystalline body. The filtered liquid, which was brown with a greenish lustre, did not deposit crystals when left to stand, but on evaporation yielded yellow amorphous masses containing the substance which the author calls *Mangostin*, mixed with a large quantity of resin. This resin is very difficult to separate. The best mode of separation is to heat the filtered alcoholic solution to the boiling point, and add distilled water in small quantities from time to time till the liquid becomes opalescent. The resin, which is but sparingly soluble in cold dilute alcohol, is for the most part deposited first, at the bottom of the vessel, while the mangostin remains in solution, and separates some time after in the form of small yellow silky laminæ. Hence, if the liquid be decanted from the resinous deposit, the mangostin which afterwards separates will be tolerably pure. But to remove the resin completely, it is necessary to dissolve the mangostin in alcohol, and precipitate with subacetate of lead, suspend the resulting compound of mangostin and lead-oxide in alcohol, after thorough washing, and pass sulphuretted hydrogen through the liquid while it is kept warm. As the mangostin will not crystallise excepting from solution in dilute alcohol, the filtered solution is then mixed at the boiling heat with water till it becomes milky. The mangostin which separates out on cooling, and by evaporation of the alcohol, is still not quite pure, and must therefore be several times recrystallised from dilute alcohol.

Mangostin crystallises in thin shining laminæ of a beautiful gold-yellow colour; it is inodorous and tasteless, melts at about 190° C. without loss of water, and forms a thick dark-yellow liquid, which on cooling solidifies in a brittle, amorphous, transparent mass, and is

* Ann. Ch. Pharm. xciii. 83.

heavier than water. When heated above the melting point, it is for the most part decomposed, but part of it sublimes unaltered. On platinum-foil it burns away without residue. It is insoluble in water, but dissolves readily in alcohol and ether. The solutions have no action on litmus-paper.

Dilute acids dissolve mangostin almost completely at a gentle heat, and deposit it unchanged on cooling. Strong nitric acid converts it, with the aid of heat, into oxalic acid. Cold concentrated sulphuric acid dissolves it with partial decomposition, forming a deep yellowish-red solution, which chars when heated. Mangostin dissolves in alkalis with a yellow or brownish colour. It is not precipitated by any metallic salt, excepting subacetate of lead. With sesquichloride of iron it produces a dark greenish-black colour, which disappears on the addition of acids.

The analysis of mangostin dried at 100° agrees with the formula $C_{40}H_{22}O_{10}$:—

Calculated.			Found.		
40 C . .	240	70.17	69.64	69.63	69.74
22 H . .	22	6.43	6.66	6.37	6.44
10 O . .	80	23.40	23.70	24.00	23.82
$C_{40}H_{22}O_{10}$	342	100.00	100.00	100.00	100.00

The lead-compound of mangostin, prepared by mixing the alcoholic solutions of mangostin and neutral acetate of lead in such proportion that the mangostin was not completely precipitated on the addition of a small quantity of ammonia, gave by analysis 44.14 per cent. PbO , 38.67 C, and 3.45 H, numbers nearly agreeing with the formula $2(C_{40}H_{22}O_{10}) + 5PbO + HO$; it is not, however, always obtained of the same composition, for another sample prepared by the same method gave only 37.46 per cent. of lead-oxide.

Certain other bodies obtained from plants of the same natural family as the *Garcinia mangostana*, appear to bear some analogy to mangostin both in composition and in properties. Gamboge from *Garcinia gutta* has, according to Johnston, the formula $C_{40}H_{18}O_{21}$. According to this composition, it is possible that mangostin may be formed by oxidation of gamboge. And, in fact, gamboge treated with strong nitric acid yields a crystalline body which appears to bear a very close resemblance to mangostin.

Indian yellow (purree), which is said to be obtained from the deposit of camels' urine after those animals have eaten the fruit of *Mangostana mangifer*, consists chiefly of the magnesia-salt of euxanthic acid, whose formula is $C_{40}H_{16}O_{21}$. As this formula stands in near approximation to that of mangostin, as well as to that of

gamboge, it is possible that both these substances may be converted in the living body into euxanthic acid.

These considerations induced the author to make some experiments with euxanthic acid, whence it appears to be a conjugated compound. In fact, when it is treated with strong sulphuric acid, and the solution poured into water, euxanthone, as is well known, separates out. The liquid filtered from this deposit has the property of quickly reducing oxide of copper dissolved in potash,—a property not exhibited by either euxanthic acid or euxanthone.

On the Action of Hydriodic Acid upon Glycerine.*

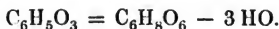
By MM. Berthelot and De Luca.

WHEN glycerine is saturated with hydriodic acid gas, and heated to 100° in a sealed tube for forty hours, and the product treated with potash and with ether, a peculiar liquid is obtained, to which the authors give the name of *Iodhydrin*. This liquid is of a golden yellow colour; syrupy; of sp. gr. 1.783; dissolves about one-fifth of its volume of water, without itself passing into the state of aqueous solution; dissolves in alcohol even when very dilute, and still more readily in ether; has a sweet taste; is not volatile; but burns away without residue, giving off vapours of iodine. Its composition is—



		Found.				Calculated.
Carbon	. . 28	28.2	29.6	—		27.9
Hydrogen	. . 4	4.7	4.6	—		4.3
Iodine	. . . —	48.3	49.3	48.4		49.2

Aqueous potash decomposes the compound at 100° , but the reaction is extremely slow. The products are, on the one hand, iodide of potassium, and a substance similar to or identical with glycerine; and on the other, a rather volatile liquid, free from iodine, soluble in ether, and having the composition—



		Found.	Calculated.
Carbon	55.2	55.4
Hydrogen	7.8	7.7

The iodine in cod-liver oil may, perhaps, be present in the form of iodhydrin, or some analogous compound.

* Compt. rend. xxxix. 748; Ann. Ch. Phys. [3] xliii. 279.

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X.—*Photochemical Researches.*

By Professor BUNSEN and H. E. ROSCOE, B.A., PH.D.

PHOTOCHEMICAL determinations which pretend to anything more than a rough approximation, are surrounded by difficulties of so considerable a nature, that up to the present time all attempts to gain a knowledge of the laws of the chemical action of light have been fruitless.

In a research on this subject which has occupied us for the space of nearly two years, we were induced to commence a careful examination of the action of light on solutions of chlorine, bromine, and iodine, as well when alone in solution, as in the presence of hydrogenous organic substances. Although these our first experiments were not carried on with a view to publication, but merely for our own instruction, in order to gain a starting-point for the solution of the question which we had proposed to ourselves, we nevertheless are obliged to make known these results, in consequence of the subsequent publication of a research on the same subject by Dr. Wittwer.* The experimental and theoretical results found by Dr. Wittwer stand in such complete and inexplicable contradiction to those obtained by us, that we have thought it necessary critically to repeat all his experiments, in order, if possible, to arrive at the cause of this difference. As, however, in this respect our endeavours have not been successful, we must confine ourselves to a scrupulous communication of our

* Pogg. Ann. xciv. 597.

experiments, from which alone the reader will be able to arrive at any satisfactory conclusion.

Dr. Wittwer undertakes to measure the chemical alterations which chlorine water undergoes when exposed to the action of light. The value of his determination depends, therefore, chiefly upon the accuracy and reliability of the method by which the amount of free chlorine in the solution is estimated. Dr. Wittwer has used the old determination of chlorine, by means of a solution of arsenious acid coloured by indigo. This method, which, as is well known, never gives very exact results, especially when the solution of chlorine is very dilute, has long since been replaced by much better processes.

In all our experiments we have employed the much more accurate and convenient iodometric method, which, even with the greatest dilution of the chlorine water, gives a degree of accuracy attainable by very few analytical processes.

The strength of the solution of iodine dissolved in pure iodide of potassium was determined by volumetric analysis* of a known weight of pure bichromate of potash dried at about 300° C.,† and gave the following values:—

	I.	II.	III.
<i>A</i>	0.0808	0.0725	0.1257
<i>n</i>	2	2	3
<i>t</i>	174.0	173.6	173.0
<i>t</i> ₁	58.3	85.0	62.2
Found α	0.0007138	0.0007077	0.0007043

As mean of these three experiments, we obtain $\alpha = 0.0007086$ for the amount of iodine contained in one burette division. In order to obtain the value of α still more exactly, the iodine solution was compared with another more concentrated normal iodine solution, prepared at a different time, and from different materials, whose mean value was found from the following experiments to be $\alpha = 0.002416$.

	I.	II.	III.
<i>A</i>	0.1755	0.1596	0.2029
<i>n</i>	4	3	4
<i>t</i>	61.1	59.2	59.0
<i>t</i> ₁	58.2	7.9	22.1
Found α	0.002412	0.002407	0.002428

* For a description of this method, and the meaning of the symbols *A*, *n*, *t*, &c., see pp. 219–236 of this volume.

† Ann. Ch. Pharm. Bd. lxxxvi. 281. In this, and in all the following experiments, the air contained in the small flask was driven out, before the decomposition began, by the addition of a few pieces of carbonate of soda to the acid solution.

To oxidise equal measures of a dilute solution of sulphurous acid, 144.0 burette-divisions of the former, and 42.1 of the latter normal solution, were required. Hence the value of the α of the first solution is found to be 0.0007063, the value directly determined being 0.0007086. The mean of these two numbers—0.0007075—is that used in the greater part of the following volumetric analyses.

In like manner we have satisfied ourselves by experiments, which we here omit, that, during the lapse of a whole year, the normal iodine solution does not undergo any change which could influence the accuracy of the experiments.

The dilution of the sulphurous acid used in these experiments cannot give rise to error, because, according to the principle of the method employed by us, a slow alteration of this acid liquid has no appreciable influence on the accuracy of the results.*

Although the accuracy of the general iodometric method has been proved by very numerous experiments, still it does not here appear superfluous to show by a few examples the degree of accuracy in the estimation of chlorine which can in this way be attained. 0.2529 grm. pure bichromate of potash was boiled with hydrochloric acid, and the liberated chlorine collected without loss in a solution of iodide of potassium. The analysis of this solution gave—

$$n=5 \quad t=62.0 \quad t_1=51.5 \quad \alpha=0.002504.$$

This gives 0.18089 grm. of chlorine: the amount of chlorine equivalent to the salt employed is 0.18091. We cite another experiment on the density of chlorine gas, made according to the iodometric method by Dr. Landolt. A current of pure and dry chlorine was passed through a tube drawn out at either end, until all atmospheric air was expelled, and then, after observation of the barometer and thermometer, the tube was closed by pressing two caoutchouc joinings at each end, and opened under a solution of iodide of potassium, in which the liberated iodine was estimated. The experiment gave—

Capacity of the tube, 31.050 cub. cent. ;

Temperature of the gas, 22° 7 C. ;

Height of barometer at 25° 4 C., 0.7567^m.

$$n=2 \quad t=31.9 \quad t_1=0.3 \quad \alpha=0.005069.$$

* We consider this peculiarity of our method to be one of its great merits, and cannot, therefore, agree with Mohr (Ann. Ch. Pharm. Bd. xciii. Heft 1), who abandons this improvement, and, for sake of convenience, remodels the process according to the old volumetric method. Still less to be recommended is his proposal, in the same memoir, to determine the free chlorine directly, without previous addition of iodide of potassium. In this case an entirely inaccurate result is obtained, as is generally the case when the separation of the iodine takes place in mixed liquids, instead of, as the method describes, in a solution of iodide of potassium.

hence 28.439 cub. cent. of chlorine at 0° and 0.76^m pressure weigh 0.08997 grm. The specific gravity of chlorine, as calculated from these data, is found to be 2.446; that calculated from the atomic weight is 2.449.

These experiments, together with many others communicated in the course of this research, prove that the determination of chlorine by the iodometric method is free from those sources of error to which the old method of Gay-Lussac is known to be subject.

Entirely independent of the inaccuracies of a badly chosen method, in Dr. Wittwer's experiments, a source of much greater error lies in the non-consideration of the disturbing influences which the phenomena of gas-absorption and diffusion give rise to. Dr. Wittwer imagined that he had entirely eliminated these sources of error by dropping into his solution of arsenious acid a chlorine-water which contained only 1 to 4 parts by weight of chlorine to 1000 of water. By the simplest experiments, however, he might have assured himself that by this method not even approximate results can be obtained, for solutions of chlorine of the strength described are influenced by the phenomena of gas-absorption and diffusion in the same way as more concentrated solutions. The amount of chlorine which is liable to be lost from solutions of the above-mentioned strength by mere dropping from one vessel to another, may be seen from the following experiments:—

EXPERIMENT I.—A small glass of 9.834 cub. cent. capacity, furnished with a well-closing glass stopper, was filled with chlorine-solution, which was quickly emptied into a solution of iodide of potassium.

The volumetric analysis gave—

$$n=2 \quad t=107.3 \quad t_1=99.6 \quad \alpha=0.0005952.$$

This is equivalent to 1.945 grm. chlorine in 1000 grms. of water. The experiment repeated, with the difference that the chlorine water was slowly dropped into the solution of iodide, according to the plan adopted by Dr. Wittwer in his volumetric analysis, gave the following results:—

$$n=1 \quad t=107.2 \quad t_1=1.4 \quad \alpha=0.0005952$$

or, in 1000 grms. liquid, 1.790 chlorine.

EXPERIMENT II.—The same volume of liquid previously employed, poured quickly out, gave—

$$n=1 \quad t=107.3 \quad t_1=1.3 \quad \alpha=0.0005952;$$

or 1.792 chlorine in 1000 water. When dropped out, the amount obtained was—

$$n=1 \quad t=107.3 \quad t_1=10.8 \quad \alpha=0.0005952;$$

or 1.633 chlorine in 1000 parts of water.

EXPERIMENT III.—By quickly pouring out, the following values were obtained:—

$$n=1 \quad t=148.3 \quad t_1=56.9 \quad \alpha=0.0007075;$$

which is equivalent to 1.838 chlorine per thousand. By dropping, the same volume gave—

$$n=1 \quad t=148.3 \quad t_1=67.0 \quad \alpha=0.0007075;$$

or 1.635 chlorine per thousand.

EXPERIMENT IV.—Quickly poured out, the same volume of solution gave— $n=1 \quad t=148.2 \quad t_1=62.0 \quad \alpha=0.0007075;$
or 1.733 chlorine per thousand.

Dropped slowly, the same volume of liquid gave—

$$n=1 \quad t=148.2 \quad t_1=68.6 \quad \alpha=0.0007075;$$

or 1.601 chlorine per thousand.

The first of the following columns shows the amount of chlorine after quickly mixing; the second, after dropping slowly; and the third, the loss of chlorine during the dropping, expressed in percentage:—

I.	II.	III.
1.945	1.789	8.0
1.792	1.633	8.9
1.838	1.635	11.1
1.733	1.601	7.6

The loss of chlorine amounts, therefore, to a mean of 9 per cent.

When we consider that a loss of chlorine must ensue even in that portion which is quickly poured from the stoppered bottle, and also that a great part of Dr. Wittwer's experiments were made with more concentrated solutions than the above, it is clearly seen that the error to which Dr. Wittwer is liable from his method of experimenting is *at least* 9 per cent. of the total amount of free chlorine contained in the solution. Let us now examine the relation in which this source of error stands to the accuracy of the experiments given on page 599 of the quoted memoir.

In order to make this comparison more clear, we have arranged the

following Table, in which the first column shows the per-centage loss of chlorine which Dr. Wittwer found by exposing the chlorine solutions to the light; and the second, the loss of chlorine which, according to his theory, he should have found if his experiments had been free from observational errors.

The loss of chlorine produced by insolation, expressed in per-centage, on the amount of chlorine originally contained :—

EXPERIMENT		Found.	Calculated.
I.	. . .	28.1	28.1
"	. . .	28.0	28.1
"	. . .	27.4	28.1
II.	. . .	27.3	27.3
"	. . .	28.4	27.3
"	. . .	25.7	27.3
III.	. . .	41.2	41.2
"	. . .	42.6	41.2
"	. . .	40.9	41.2
IV.	. . .	10.4	10.4
"	. . .	11.5	10.4
"	. . .	10.4	10.4
V.	. . .	8.9	8.9
"	. . .	7.8	8.9
"	. . .	8.0	8.9
VI.	. . .	33.6	33.6
"	. . .	35.0	33.6
"	. . .	35.4	33.6
VII.	. . .	9.9	9.9
"	. . .	12.4	9.9
"	. . .	10.9	9.9

We have just shown that even the error occurring from diffusion can, on an average, amount to 9 units of the foregoing numbers, and, therefore, in a few of the experiments, is greater than the total loss from which the theory is deduced. If, under such circumstances, it is difficult to understand how Dr. Wittwer could employ so inaccurate a method, it is perfectly unintelligible how, using this method, he has arrived at results which do not in any instance show an error of more than 3 per cent. We mention another example which shows how little Dr. Wittwer has considered or removed the errors which ensue from the phenomena of the diffusion of gases. At page 608 of the memoir, we read: "The action of chlorine on the vapour of water must here be noticed. In order that water be transformed into the vapoury condition, it is well known that 1 grm. must take up 550 heat-units; but its constituent atoms, on account of this heat, are less strongly attracted together; and when chlorine acts upon the vapour in

presence of light, the action proceeds more rapidly than with liquid water."

We find the following experiments cited as proof of this opinion:—

Portions of the same chlorine-solution (of strength 3·720 per thousand) were poured into three small bottles: the first was completely filled, the second to one-half of its volume, the third to one-quarter of its volume, and the three exposed to the action of the light for the same period. The first lost 17·07, the second 32·00, and the third 48·47 per cent. of chlorine. Dr. Wittwer ascribes these differences to a change of affinity arising from the latent heat of the vapour of water; and he has not considered that an interchange must take place between the chlorine in solution, and the atmosphere of nitrogen and oxygen, which exists above the liquid; and that therefore, according to the laws of gas-absorption, the loss of dissolved chlorine is greater as the relative volume of the air to the water increases. We have repeated the experiment, differing only from Dr. Wittwer's by the circumstance that we allowed the air and chlorine-water contained in well-stoppered bottles to remain in contact during entire absence of light. After the lapse of even four hours, the influence of diffusive absorption has become so visible, as is seen from the following Table, that we must conclude that Dr. Wittwer has determined rather this action than that of the light.

TABLE I.

	Volume.	n	t_1	t	Chlorine in 1000 water.
Bottle completely filled .	18·83	5	132·0	133·2	4·717
Ditto half filled . . .	26·28	6	112·0	133·0	4·341
Ditto quarter filled . .	11·42	2	12·5	129·0	3·576
Ditto ditto	10·00	2	38·0	128·7	3·650

The bottles were analysed four hours after filling: the amount of iodine contained in one burette-division was $\alpha = 0·0005952$. The bottle which was half filled lost, therefore, by standing four hours in the dark, 8 per cent. of its amount of chlorine; the two filled to a quarter of their volume lost 22·6 and 24·2 per cent. The cause of this considerable loss of chlorine might be ascribed chiefly to the concentration of the solution. We have, therefore, made a set of similar determinations with dilute solutions of chlorine; but in this, as in the former case, a considerable loss of chlorine was obtained.

TABLE II.

The solutions stood in the dark for 4 hours after filling; $\alpha = 0.0005952$.

	Volume.	n	t	t_1	Chlorine in 1000 parts.
Bottle filled full . . .	18.83	1	189.0	18.8	1.503
Ditto half filled . . .	23.80	2	189.0	170.8	1.448
Ditto quarter filled . . .	10.20	1	189.0	106.0	1.353

TABLE III.

The solutions stood in the dark for 15 hours after filling, $\alpha = 0.0005952$.

	Volume.	n	t	t_1	Chlorine in 1000 parts.
Bottle filled full . . .	18.83	1	182.0	15.3	1.475
Ditto half filled . . .	29.55	2	182.0	119.3	1.377
Ditto quarter filled . . .	10.60	1	181.0	106.0	1.177
Ditto ditto	12.15	1	183.8	98.0	1.174

The bottles filled to one-half lost, therefore, 3.66 and 6.64 per cent. of chlorine; those filled to one-quarter lost 9.98, 20.2, and 20.4 per cent. respectively.

If we now remember that, by dropping the chlorine-water into the normal solution, Dr. Wittwer must have had a still greater loss of chlorine, there can be little doubt concerning the amount of reliance to be placed in the experimental results which he has obtained.

We have, in our experiments, eliminated these large errors ensuing from gas-absorption, by insulating the chlorine-water contained in hermetically sealed tubes in which the volume of the air to that of the liquid employed was inappreciably small. Equal lengths of the same glass tube carefully cleaned, and as free as possible from irregularities, of about 18 millimetres diameter, were drawn out to fine long points at each end. All these tubes were then dipped into a deep vessel containing a perfectly well-mixed chlorine* solution, until the upper end of the tube just appeared above the surface of the liquid. The chlorine water which rises from the bottom of the vessel thus comes in contact with the air of the tube for scarcely a single

* The chlorine solutions employed in all these experiments were prepared and afterwards preserved in a room from which all daylight was excluded.

second, and without the slightest agitation. After a small ball of wax had been pressed on the end which rose out of the liquid, the whole tube was withdrawn from the solution, and, by means of the blowpipe, hermetically closed at both ends. A small bubble of air remained above the liquid, large enough to prevent the tube from bursting by any subsequent alteration of temperature. The tube, which was weighed before the experiment, was, after filling, again weighed (by candle-light), together with the ends melted off before the blowpipe, and the difference of these two weights gave the amount of chlorine-water contained in the tube. By this mode of filling the tubes, the chlorine-water comes in contact for scarcely a second with a perfectly undisturbed column of air of only 250 square millimeters surface, and is then immediately prevented from further contact by being hermetically closed. We are thus perfectly sure that the disturbing influences of diffusion are fully eliminated. In order to avoid the same source of error during the analysis, the tube was held vertically, and its lower end broken under the iodide of potassium solution, and afterwards the upper one also opened, so that the chlorine-solution flowed into the iodide without coming in contact with the outer air. The chlorine-solution which remains on the inner surface of the tube is easily collected by washing out with a few drops of iodide-solution. The weight of chlorine (C) equivalent to the amount of liberated iodine is found, according to the method described by one of us in the *Ann. Chem. u. Pharm. Bd. lxxxvi. 265,** by means of the following formula:

$$C = \frac{Cl}{I} a(nt - t_1)$$

After these remarks we proceed to a critical examination of Dr. Wittwer's research. The starting-point and basis of all the conclusions contained in the memoir are found in the following sentence (p. 598):—

“By equal amounts of light, the quantity of hydrochloric acid formed is proportional to the strength of the chlorine-water.”

The supposition of such a proportional action appears, even from a theoretical point of view, in the highest degree improbable. It would require the further assumption that the chemical attraction which the chlorine exerts on the particles of hydrogen of the water is independent of the chemical attractions of the remaining bodies either already present or formed during the decomposition; whilst daily occurring examples teach us that affinity must be considered as the resultant, not only of the attractions of the combining molecules, but

* See also page 219 of this volume.

also of all those present within the sphere of the chemical action; and that the magnitude of the chemical affinity is changed according to the relative number and material differences of the molecules,—dependent, however, upon laws which are as yet quite unknown. Nitrogen in the free state is certainly one of the most indifferent bodies known, and still the mere presence of this substance is sufficient to change the affinity of oxygen to hydrogen to such an extent that, in order to induce the combination of the latter gases, it is necessary to raise their temperature to a very different degree than that required if oxygen and hydrogen be alone present: an exactly similar action is found to take place in mixtures of all gases. The numberless phenomena which we class under the term “Catalysis,” are merely special cases in which this general action of affinity is rendered more strikingly evident. The consideration of phenomena of this kind makes it at once unlikely that the force with which chlorine decomposes water should neither be influenced by the volume of the water present, nor by the interchange which takes place between the water and the chlorine and oxygen and hydrochloric acid formed during the decomposition.

Dr. Wittwer has so little considered the action of these causes on chemical affinity, that he states that *the presence of hydrochloric acid is indifferent*, and specially mentions (p. 611) that he has convinced himself, by various experiments, of this indifference. The following facts will sufficiently show how far this statement is at variance with the truth. The gas obtained by electrolysis of pure concentrated hydrochloric acid, evolved from poles of pure carbon, consists, as one of us has shown, of exactly equal volumes of chlorine and hydrogen. When this gas, freed from all trace of hydrochloric acid by passing through water, is then dried over chloride of calcium, and collected with the necessary precautions, the affinity of the two gases is such, that volumes from 50 to 60 cub. cent., when exposed, even on dark days, to the diffuse light of a room, unite with explosion. The same gas collected over tolerably concentrated hydrochloric acid may be exposed to the direct rays of the sun, without any fear of explosion occurring, the combination taking place gradually. Here, then, we have a case in which the diminution of the force of affinity of chlorine, owing to the presence of hydrochloric acid, is most clearly shown. It is now not difficult to prove that, in the decomposition of water by chlorine, the affinity of the latter to hydrogen is altered by the formation of hydrochloric acid. Nearly two years ago we filled a glass tube of 82.3 cub. cent., containing about a gramme of water, with chemically pure chlorine, and closed it hermetically before the blowpipe. This tube

was exposed to the direct rays of the sun, and to diffused light, for the space of more than twenty months, without appreciably changing its colour; and after this period it was opened under a tolerably concentrated solution of potash. The amount of non-absorbed gas was found to be only 2·4 per cent. of the chlorine employed. From this experiment it may be concluded that the affinity of chlorine to hydrogen becomes inappreciably small as soon as a certain amount of hydrochloric acid is formed. The following numerical data show the great retarding influence which hydrochloric acid exerts upon the decomposing force of chlorine on water :—

TABLE IV.
Time of Insolation, 1 hour direct sunlight.

Pure Chlorine Water.			Chlorine Water with 10 per cent. Hydrochloric Acid.	
$\alpha=0\cdot0007075$	Before insolation.	After insolation.	Before insolation.	After insolation.
Weight of solution in grammes	29·057	29·373	27·463	28·601
t	150·5	135·7	133·2	135·7
t_1	11·4	95·4	24·6	22·6
n	1	1	1	1
Chlorine in 1000 parts	1·017	0·271	0·782	0·782
Of 100 chlorine decomposed	0·0	73·4	0·0	0·0

TABLE V.
Exposed for 6 hours to direct and diffuse sunlight.

Pure Chlorine Water.			Chlorine Water with 10 per cent. HCl.	
$\alpha=0\cdot0007075$	Before insolation.	After insolation.	Before insolation.	After insolation.
Weight of solution taken	29·001	27·832	27·463	29·378
t	133·3	8·4	133·2	132·5
t_1	115·0	7·8	24·6	17·8
n	2	1	1	1
Chlorine in 1000 water	1·0338	0·00426	0·7820	0·7720
Of 100 chlorine decomposed	0·0	99·6	0·0	1·3

TABLE VI.

Insolated 1 hour in diffuse light, and afterwards 30 minutes in direct sunlight.

Pure Chlorine Water.			Chlorine Water with 3 per cent. Hydrochloric Acid.	
$\alpha = 0.0007075$	Before insolation.	After insolation.	Before insolation.	After insolation.
Weight of solution employed	29.831	29.484	28.560	29.804
t	108.8	107.1	108.7	107.1
t_1	62.0	102.0	92.0	77.2
n	3	3	3	3
Chlorine in 1000 water . .	1.753	1.471	1.621	1.620
Of 100 chlorine decomposed	0.0	16.1	0.0	0.0

TABLE VII.

Insolated in 1 hour diffuse, and 30 minutes direct sunlight.

Pure Chlorine Water.			Chlorine Water with 3 per cent. Hydrochloric Acid.	
$\alpha = 0.0007075$	Before insolation.	After insolation.	Before insolation.	After insolation.
Weight of chlorine water . .	29.781	32.131	27.185	31.761
t	108.6	107.1	108.6	107.0
t_1	85.4	97.0	1.0	87.2
n	2	2	1	2
Chlorine in 1000 water . .	0.8750	0.7213	0.7825	0.7893
Of 100 chlorine decomposed .	0.0	17.6	0.0	0.9

From Table IV. it is seen that a solution of chlorine exposed to direct sunlight during one hour lost 73.4 per cent. of chlorine. The same solution to which 10 per cent. of hydrochloric acid was added, was not the least altered by exposure during the same time. According to Table V., a solution of chlorine, exposed for upwards of six hours to direct and diffuse sunlight, lost 99.6 per cent. or nearly the total amount of contained chlorine. By addition of 10 per cent. of hydrochloric acid, the action during the same time is reduced to 1.3 per cent. In Tables VI. and VII., chlorine water, exposed to diffuse light for 1 hour, and to the sun's direct rays for 30 minutes, lost from 16.1 to 17.6 per cent. of chlorine; mixed with 3 per cent. of hydrochloric acid, and subjected to a similar insolation, the amount of chlorine remained unaltered.

In order to give a still further confirmation of the subject under

consideration, we mention one other experiment, made a year ago, which shows that the decomposing force which bromine exerts upon water containing a small quantity of alcohol, is considerably altered by the presence of hydrobromic acid.

TABLE VIII.

Alcoholic Bromine Water.			Ditto with $\frac{1}{2}$ to $\frac{3}{4}$ per cent. Hydrobromic Acid.			
	I.	II.	III.	IV.	V.	VI.
Time of insolation	—	30'	—	30'	45	60'
Weight of solution in grammes	200	200	200	200	200	200
t	47.0	46.2	47.0	46.2	46.2	44.4
t_1	19.4	32.8	19.4	21.5	24.0	21.7
n ($\alpha=0.0022593$)	1	1	1	1	1	1
Bromine in 1000 water	1.965	0.954	1.966	1.759	1.581	1.617
Loss of bromine per cent. . . .	0.0	51.5	0.0	10.5	0.0	17.75

The lowest horizontal division in the Table shows that the loss of bromine in the liquid free from acid, during an exposure of thirty minutes, amounted to 51.5 per cent.; that the loss, during the same period, of the solution containing only 1 per cent. of hydrobromic acid, was only 10.5 per cent., and during a period twice as long, 17.75 per cent.

From all these experiments, there cannot, therefore, be the slightest doubt that the hydrochloric acid produced by the decomposition of water by chlorine exerts a very strong retarding action on the affinity of chlorine for hydrogen.

We are unable to conceive what circumstances can have induced Dr. Wittwer* to ignore these plain facts, as no single one of his "often repeated" experiments on this subject is given in his memoir. Dr. Wittwer's fundamental experiments are, however, still more inexplicable. It is difficult to conceive how a mode of experiment which is accompanied by a mean error of 9 per cent. can give results whose inaccuracy scarcely reaches the error incurred by the weighing; and how these numbers can stand in perfect harmony with a hypothesis which, as our experiments show, has no application to the decomposition of chlorine-water. Dr. Wittwer's theory starts from the supposition that aqueous solutions of chlorine lose, by equal insolation, an equal fraction of the originally contained chlorine,—with

* Dr. Wittwer actually proposes to employ a solution of chloride of lime, decomposed by hydrochloric acid, as an absolute measure of the chemical rays.

the limitation, however, that the layer of chlorine water does not exceed a certain thickness.

To satisfy this condition, the following experiments, which we have arranged in a tabular form, were conducted with hermetically sealed tubes of 20 millimeters diameter, and, therefore, smaller than the stoppered bottle employed by Dr. Wittwer. In spite of this, our experiments do not show even approximation to the law founded by Dr. Wittwer. The theory requires that the per-centage decomposition remain constant for all concentrations of the chlorine solutions; the results of the following Tables show that in every case a different per-centage decomposition was obtained.

From Table IX. 11.94 and 15.7 per cent.

"	X.	43.0	"	37.5	"	
"	XI.	45.9	"	53.6	"	and 40.4 per cent.
"	XII.	68.6	"	75.3	"	62.8 "
"	XIII.	81.8	"	88.2	"	77.7 "
"	XIV.	73.3	"	58.7	"	

TABLE IX.

Pure Chlorine-water exposed to diffuse light for 69 hours.

$\alpha = 0.0007075$	Before insolation.	After insolation.	Before insolation.	After insolation.
Weight of solution	32.786	27.879	29.781	28.142
t	144.5	145.5	108.6	145.0
t_1	9.0	81.0	85.4	40.0
n	2	2	2	1
Chlorine in 1000 water	1.6884	1.4896	0.8752	0.7378
Of 100 chlorine decomposed	0.0	11.94	0.0	15.7

TABLE X.

Pure Chlorine-water exposed to diffuse light for 168 hours.

$\alpha = 0.0007075$	Before insolation.	After insolation.	Before insolation.	After insolation.
Weight of solution taken	27.199	25.685	30.525	27.570
t	136.8	135.2	136.2	135.2
t_1	25.0	1.3	3.0	60.0
n	2	1	1	1
Chlorine in 1000 water	1.8074	1.0309	0.8629	0.5394
Of 100 chlorine decomposed	0.0	43.0	0.0	37.5

TABLE XI.

Pure Chlorine-water exposed 1 hour to direct sunlight.

$\alpha = 0.0007075.$	Before insolation	After insolation	Before insolation	After insolation	Before insolation	After insolation
Weight of solution .	24.070	25.158	27.020	27.156	27.537	21.378
t	110.0	109.8	109.0	109.8	109.8	109.8
t_1	5.5	36.0	75.5	43.4	27.9	71.9
n	3	2	2	1	1	1
Chlorine in 1000 water	2.669	1.4432	1.0427	0.4835	0.5881	0.3506
Of 100 chlorine decomposed	0.0	45.9	0.0	53.6	0.0	40.4

TABLE XII.

Pure Chlorine-water exposed for 1 hour 30 minutes to direct sunlight.

$\alpha = 0.0007075.$	Before insolation	After insolation	Before insolation	After insolation	Before insolation	After insolation
Weight of chlorine water	24.070	27.204	27.020	27.889	27.537	28.433
t	110.0	122.7	109.9	13.4	109.8	13.2
t_1	5.5	7.5	79.5	4.4	27.9	8.2
n	3	1	2	3	1	3
Chlorine in 1000 parts water	2.669	0.8374	1.0268	0.2538	0.5880	0.2184
Of 100 chlorine decomposed	0.0	68.6	0.0	75.3	0.0	62.8

TABLE XIII.

Pure Chlorine-water exposed for 2 hours to direct sunlight.

$\alpha = 0.0007075.$	Before insolation	After insolation	Before insolation	After insolation	Before insolation	After insolation
Weight of chlorine water	24.070	25.716	27.020	25.387	27.537	23.110
t	110.0	109.5	109.9	13.2	109.8	13.2
t_1	5.5	50.9	79.5	10.9	27.9	11.1
n	3	1	2	2	1	2
Chlorine in 1000 parts water	2.669	0.4506	1.0268	0.1208	0.5881	0.1309
Of 100 chlorine decomposed	0.0	81.8	0.0	88.2	0.0	77.9

TABLE XIV.

Pure Chlorine-water exposed for 2 hours to the direct sunlight.

$\alpha = 0.0007075.$	Before insolation.	After insolation.	Before insolation.	After insolation.
Weight of chlorine water . .	27.075	29.373	29.300	25.755
t	150.5	135.7	133.1	135.6
t_1	11.4	95.4	57.0	108.0
n	1	1	1	1
Chlorine in 1000 parts water .	1.0166	0.2713	0.5136	0.2119
Of 100 chlorine decomposed .	0.0	73.3	0.0	58.7

If we suppose, as is most simple, that the decomposing force of the light is proportional, firstly to the length of exposure and to the intensity of the light, and secondly to the mass of decomposing substance present in the unit of volume, it is seen from the foregoing Tables that the affinity of the chlorine to the hydrogen of the water first increases by diminution of the amount of contained chlorine, then attains a maximum, and afterwards again diminishes. Numerous instances of such a mode of action of affinity will occur to every chemist.

Although, after all these explanations, it must appear almost unnecessary further to examine Dr. Wittwer's experiments, we have repeated the experiment cited in the research at pages 600 and 601. Our only object in continuing this examination was the wish to leave no means untried which by any chance could lead to an explanation of the above contradictions. Here, also, as might be expected, our attempts were fruitless. In order more fully to establish his supposition that, by equal intensities of light, the amount of hydrochloric acid produced is proportional to the contained chlorine, Dr. Wittwer shows by experiments (which again, in spite of the source of error above mentioned, agree precisely with the theory to be proved) that the alteration of the chlorine solution is proportional to the product of the amount of light into the strength of the chlorine-water, and the time of exposure. In this experiment he determined the loss which a solution of chlorine suffers by exposure for 10, 20, 30, and 40 minutes each, during a constant intensity of light. From S the original strength of the chlorine-water, and s the strength after insolation during a time t , he finds the intensity I of the light for the whole time during which his experiment lasted; and his numbers agree as far as the third decimal figure.

On page 601 of Dr. Wittwer's memoir, we find the following experiment:—

<i>t</i>	<i>s</i>	<i>I</i>
10' . . .	2·1659 . . .	0·11607
20' . . .	1·9164 . . .	0·11923
30' . . .	1·7279 . . .	0·11398
40' . . .	1·5239 . . .	0·11690
50' . . .	1·3660 . . .	0·11541

The first column expresses the time of insolation; the second, the amount of chlorine contained in 1000 parts of liquid which, before insolation, contained 2·4324 chlorine in 1000 parts. We have already shown that the mean error which is caused by diffusion during the dropping out of the chlorine-solution, amounts to about 9 per cent. Supposing, now, that this error is twice as large as that actually present,—that is, suppose that the real error amounts to 4·5 per cent.,—the inaccuracy to which Dr. Wittwer is then liable is so large, that in his first observation, for example, he may just as probably have obtained the number 0·16206, instead of 0·11607, as the value of *I*.

In order to avoid all disturbing influences in our experiments, we conducted them precisely under the outward circumstances mentioned by Dr. Wittwer: we also chose for our insolation the noon of a cloudless day. The probability that the value of *I* remained constant during our determination, is four times larger than is the case with Dr. Wittwer's experiment, as we conducted the insolation according to a system which required that the light should remain constant for a period only one-fourth so long. The following is a description of the method which we employed:—Suppose that five tubes containing chlorine-water be exposed to the same amount of light during varying lengths of time; for instance, the first for 18 minutes, the second for twice 18 minutes, the third for three times 18 minutes, and so on; all the tubes are exposed at the same moment, and after the lapse of every 18 minutes each one of the tubes may be covered. As the first tube was insolated for only 18 minutes, the last, on the other hand, for 90 minutes, it is necessary that the amount of light remain constant for 90 minutes. If, on the contrary, all the tubes be exposed to begin with together, but the first insolated for 3 minutes, the second for 6 minutes, the third for 9 minutes, the fourth for 12 minutes, the fifth for 15 minutes, and if this regular opening and covering of the tubes be repeated for each 18 minutes, the light is only required to remain constant for 18 minutes, and gives results as

accurate as the other method, which requires a constant source of light of 90 minutes duration.

In the following experiment, 5 sealed tubes of chlorine-water, of the strength $S=0.2641$ per cent. of chlorine, were insolated according to the preceding system, so that the exposure lasted from 18 minutes up to 90 minutes. The required condition for a constant value of I was therefore given when the alteration of the intensity during every 18 minutes is taken as inappreciable; whereas in Dr. Wittwer's experiment a constant intensity for 1 hour 10 minutes is necessary.

TABLE XV.

Duration of the experiment 1 hour 30 minutes.

Pure Chlorine-water, $\alpha=0.00059018$.

Length of insolation.	Not insolated.	18' in sunlight.	36' in sunlight.	54' in sunlight.	72' in sunlight.	90' in sunlight.
Weight of chlorine-water	24.248	25.205	24.566	23.538	23.448	23.311
t	125.5	125.5	126.0	126.0	126.0	126.0
t_1	113.8	57.1	1.0	77.3	27.5	61.4
n	4	3	2	2	1	1
Chlorine in 1000 parts water . .	2.6409	2.0904	1.6854	1.2244	0.69297	0.4752
Value of I	0.0	0.0130	0.0125	0.0142	0.0186	0.0195

The lowest line of the preceding Table contains the values of I calculated from each experiment; it is here seen that these numbers are anything but constant, varying from 0.013 to 0.019.

In reviewing the results of our experiments, we find the following conclusions justified:—

1. *The products formed by the photochemical decomposition of chlorine-water exert a retarding action on the amount of the original affinity of the chlorine.*
2. *The decomposing action of chlorine on water is therefore neither proportional to the length and intensity of the insolation, nor to the strength of the chlorine-water.*

As the photochemical action is thus accompanied by a simultaneous change in the affinity, dependent on laws altogether unknown, it would be a completely hopeless task to endeavour to arrive at the

laws of the chemical action of light by the insolation of chlorine-water. We have, therefore, for upwards of a year given up all attempts of this kind, and have had recourse to another method, by help of which we have succeeded in establishing a series of very simple relations exhibited by the chemical action of light. The simple law which governs these interesting relations we shall communicate in our next paper on this subject.

XI.—*On the Colour of Chloride of Copper in different States of Hydration.*

By J. H. GLADSTONE, PH.D., F.R.S.

THERE are two theories respecting the aqueous solutions of haloïd salts :—the one maintains that the compound of a metal and a halogen dissolves as such in the water; the other, that it becomes a compound of the metallic oxide and the hydracid, which is also dissolved in the liquid. One of the arguments adduced in support of the latter theory is, that certain salts, such as the chloride or bromide of copper, or the chloride of cobalt, change colour on dissolving in water, and assume a tint which is supposed to belong to the oxide. It happened that in my recent investigation of circumstances that modify the action of chemical affinity, I examined the changes of colour which take place when hydrochloric acid or a soluble chloride is added to a solution of a blue salt of copper. This led to an examination of the chloride itself; and the observations then made have been extended, with a view to determine, if possible, how far the change in colour may really lend support to the theory in question. The following are the facts with which this examination has made me acquainted.

Chloride of copper exists in a solid form in two conditions: the one anhydrous, the other containing the elements of water.

The anhydrous salt.—This is amorphous, and of a yellowish brown colour, whether produced by the combustion of copper in chlorine, or by heating the hydrated compound. Its composition has been determined by Berzelius and J. Davy to be CuCl .

The hydrated salt.—This exists either in an amorphous or a crystalline form, according to the mode of preparation.

If anhydrous chloride of copper be exposed for a few minutes to

the ordinary atmosphere, it begins to change from yellowish-brown to pale bluish-green. This will go on till the whole mass becomes a bluish-green powder, which is dry to the touch, not deliquescent in ordinary states of the atmosphere, and devoid of crystalline form, even when viewed under the microscope. Professor Graham believes this to be the hydrate $\text{CuCl} \cdot 2\text{HO}$.* An experiment of mine confirmed this view. 0.960 grm. of anhydrous chloride of copper, on exposure, increased in weight to 1.224 grm.: theory requires 1.216 grm.

If the oxide or carbonate of copper be dissolved in hydrochloric acid, and the solution evaporated nearly to dryness, bluish-green crystals separate. Their form has been determined as that of a right-angled four-sided prism. They are more deliquescent than the amorphous hydrate. No complete analysis of this salt seems to have been published. Its received formula $\text{CuCl} + 2\text{HO}$ rests on the observation of Professor Graham, that the crystals give off 21.53 grm. of water when strongly heated.

- I. 1 grm. of the crystals, dried at a temperature somewhat under 100°C ., gave off 0.212 grm. of water when heated more strongly, and yielded 0.473 grm. of oxide of copper.
- II. 1.22 grm. gave 2.003 grms. of chloride of silver.
- III. 1 grm. of another preparation gave off 0.214 grm. of water when heated, and afforded 0.472 grm. of oxide of copper.
- IV. 0.5 grm. of the same yielded 0.830 grm. of chloride of silver.

These results give percentage numbers nearly coincident with those deduced from the above formula.

	Found.		Calculated.
	1st preparation.	2d preparation.	
Copper . . .	37.84	37.76	37.47
Chlorine . . .	41.01	41.06	41.45
Water . . .	21.20	21.40	21.08
	<hr/> 100.05	<hr/> 100.22	<hr/> 100.00

It is evident that this green salt may either be $\text{CuCl} + 2\text{HO}$, or $\text{CuO}, \text{HCl} + \text{HO}$. If the latter, it might be reasonably expected that some difference would show itself between the two atoms of hydrogen and oxygen; but my observations, though specially

* Phil. Trans. 1837, p. 71.

directed to the point, have failed to remark any. The brown salt appears to assume the two atoms at once; neither is there any intermediate stage in the dehydration of the green salt. When the crystals are heated to about 90°C . (194°F .), they begin slowly to give off water, shrink, and assume at once the brown colour. If the temperature be raised a little above 100°C ., the water is given off rapidly. If strong sulphuric acid be added to the green crystals, or to a strong aqueous solution, the brown salt is instantly produced. There appears, then, to be no ground for supposing that the difference of colour between the anhydrous and the hydrated salt depends upon the conversion of the latter into hydrochlorate of the oxide of copper.

Effect of solution.—If an equal weight of water be added to the pure green salt, it dissolves, giving a clear solution of a deep green colour. On the addition of more water, a gradual change of colour occurs, as indicated in the annexed table:—

Composition of Solution.						Colour.
1	part	crystal.	chloride of copper	+ 1	part water	Deep green.
"	"	"	"	+ 2	"	Bluish green.
"	"	"	"	+ 3	"	Still blue.
"	"	"	"	+ 4	"	Nearly pure blue.
"	"	"	"	+ 5	"	Blue.

Oxychloride of Copper.—It may be as well to remark, in this place, that on dissolving most specimens of crystallised chloride of copper, a white subsalt separates, not when the solution is so strong as to appear green, but when it passes from green to blue. This deposit was observed in one instance to be as much as $\frac{8}{100}$ ths of the whole weight of the salt, though usually it is considerably less than that. When dry it is a pale green powder, which remains unaltered, though heated up to 215°C . (419°F .), but when almost at incipient redness, it gives off both water and chlorine, and is converted into a black mixture of oxide and dichloride of copper. The following analyses were made:—

- I. 1 grm. of the subsalt dried at 100°C ., and dissolved in dilute nitric acid, yielded 0.734 grm. of oxide of copper, and 0.812 grm. of chloride of silver.
- II. 1 grm. of a different portion gave 0.760 grm. of oxide of copper, and 0.829 grm. of chloride of silver.
- III. 0.535 grm. of another preparation gave 0.397 grm. of oxide of copper.

These numbers reckoned to 100 parts represent—

	I.	II.	III.
Copper	58.72	60.80	59.36
Chlorine	20.08	20.51	—

The proportion of the copper to the chlorine appears thus to be as three atoms to one, and, though the salt is evidently somewhat irregular in its composition, it approaches nearer to the oxychloride, CuCl , 2CuO , HO , than to any other of the eight or nine that have been described by previous investigators.

Copper	61.34
Chlorine	22.68
Oxygen and hydrogen	15.98
	<hr/>
	100.00

It is probably this oxychloride with the admixture of a varying quantity of one containing more of the elements of water. Whether the constitution of this salt be as above written, CuCl , 2CuO , HO , or 3CuO , HCl , there seems nothing to decide.

This oxychloride dissolves in a strong solution of pure chloride of copper; and the crystals derived from such a solution retain the form of the pure salt, but are of a yellowish-green instead of a bluish-green tint; when dissolved in water, they give an abundant deposit, and they contain a deficiency of chlorine,—indeed, in a case submitted to analysis, only 39.75 per cent. The great disparity of tint observed in different specimens of crystallised chloride of copper seems to arise generally from the varying amount of oxychloride they contain, though an excess of acid will also cause the crystals to assume a yellowish colour. Crystals that dissolve without deposit may be obtained from an impure salt by repeated solution, filtration, and recrystallisation, though, perhaps, the chloride thus obtained is never absolutely free from subsalt. The best method of obtaining pure crystals is to start with a very acid solution. If strong hydrochloric acid, not in excess, be poured upon the oxychloride, a solution results, which, on dilution, deposits the subsalt.

Change of colour.—It has already been observed, that the solution from which the oxychloride has separated changes gradually from a deep green to a clear blue. The question arises,—Does this change of colour depend upon some action of the water, or of the elements of it; or is it in some way a mere physical result of the solution?

In the hope of determining this matter, the action of other solvents

was tried. It was found that brown anhydrous chloride of copper dissolves in absolute alcohol of a yellowish-green colour, and that it does not assume a bluish tint on any amount of dilution with the same solvent. This is the case also when either the bluish-green or yellowish-green crystals are dissolved in absolute alcohol, or even in strong spirits of wine,—the alcohol appearing to abstract the water from the hydrated salt. Even the addition of alcohol to a moderately strong aqueous solution heightens the green, imparting a yellowish tint to it. If the crystals contain oxychloride, alcohol does not cause its separation. The addition of water in considerable quantity to the alcoholic solution causes a production of the blue colour, and a deposition of any subsalt that may be present. If a solution of the anhydrous chloride in absolute alcohol be evaporated down, it shows little or no tendency to crystallise, but becomes an almost black viscid mass, which, however, on standing for some hours, becomes filled with tufts of yellowish-brown crystals.

Ether in like manner dissolves chloride of copper, giving an intense yellowish-green solution, which also does not alter in the character of its colour when diluted with any amount of additional ether.

The change from green to blue depends, then, upon the water; but is it because the salt is converted into hydrochlorate of oxide of copper, or because it forms a higher hydrate than exists in the crystals? The following observations may possibly afford some grounds for forming an opinion.

Hydrochloric acid imparts a bright yellowish tint to the green solution of chloride of copper. On dilution with water, such a mixture also assumes a blue colour, but it requires much more water than the neutral salt does. The following table will exhibit the changes of tint produced during the dilution of a mixture of single equivalents of chloride of copper and hydrochloric acid. It would not dissolve completely in an equal weight of water.

Composition of Solution.					Colour.
1	part	CuCl + HCl	with 2	parts water	Dark green.
"	"	"	5	"	Bright yellowish green.
"	"	"	8	"	Bluish green.
"	"	"	12	"	Almost pure blue.
"	"	"	15	"	Blue.

During this dilution there is a gradual alteration of the colour; but the change appears to be more rapid at certain points than at others. Yet, after careful and repeated examination, I came to the belief that the effect of water is regular, and that what appears like rather sudden

transitions, is due to the difficulty of comparing solutions of different shades of colour.

If a solution containing single equivalents of chloride of copper and hydrochloric acid be diluted till it becomes blue, the addition of more hydrochloric acid will cause it to resume the green colour, and, if sufficient be added, to become of the bright yellowish tint,—the amount of greenness being regularly proportionate to the amount of hydrochloric acid present.

The compound of chloride of copper and hydrochloric acid, which may be supposed to exist in these yellowish-green solutions, does not appear to be crystallisable. If a solution of the copper salt in hydrochloric acid be evaporated, crystals separate of a bright green colour. On drying between folds of bibulous paper, these part with the adhering strongly acid liquid, and at the same time their yellowish tint is greatly reduced. A portion so prepared was dried at 80°C ., when it appeared very like the ordinary bluish-green crystalline salt. It weighed 1.240 grm. At a higher temperature, it gave off water, and a little hydrochloric acid. After being heated at 150°C ., it was converted into apparently the anhydrous chloride, and weighed 0.969 grm. The same amount of $\text{CuCl}, 2\text{H}_2\text{O}$ would have given by calculation 0.979 grm.,—a quantity scarcely exceeding that actually found, so that the hydrochloric acid attached to the crystals must have been a mere trace. Another experiment gave a similar result. That the brown powder left on heating this was really CuCl was proved by a determination of the copper.

0.531 grm. yielded 0.318 grm. of oxide of copper; which gives the following percentage:—

	Found.	Calculated.
Copper	47.83	47.48

Some other chlorides,—such as chloride of sodium and chloride of ammonium,—produce the same yellowish colour in solutions of chloride of copper as hydrochloric acid does; whilst others, such as chloride of calcium, do not affect it. Some of these double chlorides have been crystallised and described.

The colour of a solution of chloride of copper alters much with the temperature. If it be heated, it becomes gradually yellower, even if previously diluted to such an extent as to be perfectly blue. Indeed, it was found that 2.5 grm. of the crystallised salt, when dissolved in three ounces of water, so that the blue colour was pale, assumed a distinctly green shade when the solution was heated to the boiling point. The same occurs in the presence of hydrochloric acid. On

cooling again, the yellow tint gradually disappears. This action also is not confined to temperatures above the ordinary: a green solution of the chloride placed in a frigorific mixture becomes blue.

The remarks here made upon solutions of pure salt in distilled water apply equally to the salt when produced by double decomposition:—for instance, to a mixture of sulphate of copper and chloride of sodium, though, of course, in such a case the blue colour of the sulphate still unaltered interferes with the result. The addition of sulphuric acid to a somewhat dilute solution of chloride of copper tends to produce the bright green, evidently from the liberation of some of the hydrochloric acid, though blue sulphate must be produced at the same time.

The following are the inferences which I have drawn from these experiments, and which I now submit to the consideration of chemists:—

Every observation made on this salt is perfectly explicable on the supposition that the proper colour of chloride of copper is brown, and that it forms hydrates which are green or blue, just as the white sulphate of copper becomes blue when hydrated. Some of the facts, too, are *more* easily explained on this view.

Thus it is hard to imagine that if green be the colour of CuCl , and blue that of CuO , HCl , the addition of more HCl to the latter should render it green; while it is readily conceivable that the hydrochloric acid should replace a portion of the water in the blue hydrated chloride of copper, and form a green double chloride, CuCl , HCl . The action of heat is in harmony with what we know of its action on unquestionable cupric hydrates: thus, the hydrated oxide of copper, when heated in the presence of any amount of water, loses its combined water and its blue colour.

If the change of colour is to be taken as evidence that crystallised chloride of copper becomes, when treated with a considerable amount of water, CuO , HCl , a parity of reason should lead us to conclude that the bluish-green crystals contain none of the yellowish-brown CuCl ; yet, if we suppose that these crystals actually contain the oxide, we can give no consistent account of the subsequent change of colour on solution.

Perhaps none of these observations are decisive on the point; yet it appears to me that this examination of the chloride of copper has gone far to show, that, instead of its furnishing an argument in favour of the supposition that haloid salts are decomposed by water, it leads towards the opposite conclusion.

There are three incidental remarks which may be appended.

Those who hold the binary theory of salts, and contend for the resolution of the chloride into the hydrochlorate, must consistently suppose the same when the salt-radical is a compound body: thus—

If	NaCl in water becomes	NaO, HCl,
then	NaNC ₂ " "	NaO, HNC ₂ ,
and	NaSO ₄ " "	NaO, HSO ₄ .

Even where different salts of a base have the same colour, the same amount of the base does not give the same intensity of colour. Thus, if equal portions of oxide of copper be dissolved respectively in acetic, hydrochloric, nitric, and sulphuric acids, and equally diluted, the acetate will be found to be far deeper in colour than the nitrate, this somewhat deeper than the sulphate, and this again far deeper than the chloride. On being converted into ammoniacal salts, these four approximate more nearly, but are still far from identical in colour.

Whatever theory be preferred for explaining the changes of colour that take place during the solution of chloride of copper, the influence of mass is very apparent. It is almost self-evident that different compounds co-exist in the solution in proportions varying with the amount of water present, or of free hydrochloric acid, and that the final state of combination is the resultant of several affinities of different degrees of strength acting on the same particles.

NOTICES
OF
PAPERS CONTAINED IN OTHER JOURNALS.
BY HENRY WATTS, B.A., F.C.S.

On a Method of Volumetric Analysis of very general Application.*

By R. Bunsen.

THIS method, which is applicable to a great number of analyses depending upon oxidation and reduction, is founded on the principle of liberating a quantity of iodine equivalent to the substance which is to be determined, and estimating this iodine by means of a standard solution of sulphurous acid. The use of sulphurous acid for the estimation of iodine, which was originally proposed by Dupasquier, gives exact results, provided always that the solution of sulphurous is sufficiently dilute. Sulphurous acid and iodine, in presence of water, form hydriodic and sulphuric acids; but, on the other hand, sulphuric and hydriodic acids may react upon each other in such a manner as to yield sulphurous acid, water, and iodine. This latter reaction takes place to a greater extent as the liquids are more concentrated. Hence, when iodine is treated with sulphurous acid, this acid will not be completely oxidised unless the liquid is sufficiently dilute. Hence the necessity of using, in this process, solutions not containing more than 0.04 to 0.05 per cent. of anhydrous sulphurous acid.

The method about to be described requires three test-liquids: a solution of iodine, a solution of sulphurous acid, and a solution of iodide of potassium. To prepare the first, a quantity of iodine, as pure as can be obtained, is dried at ordinary temperatures over chloride of calcium, *g* grammes of it then weighed out between watch-glasses, and dissolved in a litre-measure by a concentrated solution of iodide of potassium, which solution must not exhibit any brown colour, either by itself, or on the addition of hydrochloric acid. If one degree of the burette contains, as usual, 0.5 cubic centimetres, the resulting

* Ann. Ch. Pharm. lxxxvi. 265; Ann. Ch. Phys. [3] xli. 339.

solution must be diluted with a quantity of water sufficient to bring the volume to $\frac{g}{0.005}$ cubic metres. Each degree of the burette will then contain 0.0025 grm. of the iodine used. But as commercial iodine, even the purest, contains traces of chlorine, it is necessary in determining the strength of the solution to take account of this impurity. For this purpose, a weighed quantity of dried iodine is dissolved in cold sulphurous acid, the solution precipitated with nitrate of silver, and the precipitate digested with nitric acid before filtration, to remove any sulphite of silver that may be thrown down at the same time. If the quantity of impure iodine used be called A , the quantities of pure iodine and chlorine contained in it, by x and y , and the precipitated chloride and iodide of silver by B ; then

$$x + y = A$$

$$\text{and } \frac{\text{Ag} + \text{I}}{\text{I}}x + \frac{\text{Ag} + \text{Cl}}{\text{Cl}}y = B$$

If we denote the ratio of the equivalents of iodide of silver and iodine, namely, $\frac{\text{Ag} + \text{I}}{\text{I}}$ by α , and the ratio of the equivalents of chloride of silver and chlorine, namely, $\frac{\text{Ag} + \text{Cl}}{\text{Cl}}$ by β , we have —

$$y = \frac{B - \alpha A}{\beta - \alpha}$$

From this value of y , we may readily calculate the quantity of pure iodine which is equivalent to a unit of weight of the impure substance. For the quantity of chlorine y , exerts the same oxidising action as the quantity of iodine $\frac{\text{I}}{\text{Cl}}y$. Hence, the chlorinated iodine A exerts the same oxidising action as the quantity of pure iodine denoted by $A - y + \frac{\text{I}}{\text{Cl}}y$; and, therefore, the quantity of pure iodine a' , which corresponds to the quantity a of the impure iodine contained in a degree of the burette, is given by the equation—

$$a' = a + \frac{a}{A} \cdot \frac{B - \alpha A}{\beta - \alpha} \cdot \left(\frac{\text{I}}{\text{Cl}} - 1 \right)$$

Of the iodine used in most of the following experiments, 1.4379 grm. gave in one experiment 2.7498 grms. iodide and chloride of silver; in another, 1.7456 grm. iodine gave 3.3251 grms. iodide and chloride of silver. Substituting these values together with $a = 0.0025$ in the last equation, we find for the quantity of *pure* iodine in a degree of the burette, from the first experiment, 0.0025246 grm., and, from the second, 0.0025318; mean: $a' = 0.0025387$.

A simpler and better method of finding the value in pure iodine of a degree of the burette, when the iodine used is impure, will be given with the volumetric analysis of chromate of potash.

If the standard iodine-solution be used at a temperature different from that at which it was prepared, an error will be committed in consequence of the change of volume of the liquid which is measured. As, however, this variation for 10° C. of temperature does not amount to more than $\frac{8}{1000}$ of the quantity of iodine to be determined (which is at most 0.2 or 0.3 grm.) it may be safely neglected with any variation of temperature that may actually occur, and the more so, as the atomic weights of the substance to be determined are generally small in comparison with that of iodine.

The measurement of this iodine-solution, which is perfectly stable, is best performed in a burette, the degrees of which correspond to 0.5 cubic centimetre of liquid. To avoid any error in reading arising from parallax, the instrument is loosely held between the thumb and forefinger, and allowed to hang down, and the level of the liquid is read off at the lower surface of the fluid meniscus, as soon as that surface coincides with a horizontal line fixed at some distance. In this manner, the reading may be performed with certainty to $\frac{1}{10}$ th of a degree, especially if the observer waits till the liquid adhering to the sides of the burette has run down sufficiently to make the level constant.

Of the second test-liquid, the dilute sulphurous acid, it is best to prepare 20 or 30 litres at a time, so that the alteration in the amount of acid produced by the action of the air during the course of an experiment may be imperceptibly small. In such a fluid mixture, the decrease of sulphurous acid in a bottle half full of air, amounts, in 24 hours, to about 1 or 2 burette degrees, so that the diminution which occurs during the three or four minutes occupied in an experiment does not exceed $\frac{8}{1000}$ of a burette degree, or 0.0002 milligramme of iodine, a quantity altogether inappreciable. To give the acid the proper degree of dilution, 20 or 30 litres of water are mixed with a small measure-glass-full of concentrated sulphurous acid; the liquid shaken; 200 burette degrees of it measured off; and this portion tested, after addition of starch, with the standard solution of iodine. If τ degrees of this solution are required to decompose the acid, and if the quantity of iodine a , contained in a burette degree, amounts to about 0.002 to 0.003 grm., then, in order to obtain the required degree of concentration, viz. about 0.03 sulphurous acid to 100 water, it is merely necessary to add to the entire liquid $\left(\frac{48}{\tau} - 1\right)$ of concentrated sulphurous from the small measuring bottle.

If $\left(\frac{48}{\tau} - 1\right)$ becomes negative, we may know that the assigned

measure has already been exceeded by the first addition of acid. The experiment must, therefore, be repeated with a smaller measure, or with less concentrated acid. As sulphurous acid oxidises by exposure to the air, the solution must be renewed every three or four days, which may be done without any trouble, as the quantity of sulphurous acid to be added to the water is known from the previous preparation. The solution should also be shaken up before being used.

The third test-liquid used in the determinations is a solution of iodide of potassium containing about 1 grm. of the iodide to 10 cubic centimetres of water. With a little practice, however, this solution may be dispensed with, a small piece of solid iodide of potassium being added in each experiment.

1. *Determination of Iodine.*—The weighed sample of iodine is dissolved in the solution of iodide of potassium contained in a capacious beaker glass, about 4 or 5 cubic centimetres of the solution being taken to 0.1 grm. of iodine. To the resulting brown solution, as many measures of the standard solution of sulphurous acid (measured in a stoppered cylinder) are added, as are required to destroy the brown colour completely, the acid which adheres to the sides of the cylinder being each time rinsed into the beaker with distilled water, and the measuring vessel subsequently washed with the normal sulphurous acid solution. The next step is to determine the quantity of iodine x , by which the sulphurous acid has been partially decomposed. For this purpose it is necessary to determine the quantity of iodine required to decompose the sulphurous acid still present in excess. This is effected by adding 3 or 4 cubic centimetres of clear and very dilute starch solution, and then dropping in the standard solution of iodine till a blue colour begins to appear. If the quantity of iodine-solution required to produce this effect is measured by t' degrees of the burette, and the quantity of iodine in one degree is x , then the quantity required to decompose the n measures of sulphurous acid added will be $x + at'$. Further, if we determine, by means of the burette, the quantity of iodine at , required to decompose 1 measure of sulphurous acid, we shall obtain the equation $x + at' = nat$, whence $x = a(nt - t')$. If the weight of the sample of iodine be A , the quantity of iodine expressed as a percentage will be

$$x = \frac{100 a}{A} (nt - t') ;$$

and if $\frac{100 a}{A} = 1$, that is, if the quantity weighed out be exactly 100 a , the equation becomes simply $x = nt - t'$: that is to say, the difference of the two measurements $nt - t'$ gives at once the percentage of iodine in the sample.

0.7979 grm. of chemically pure iodine mixed with 1.0400 grm. iodide of potassium, and tested in this manner, gave—

$$n=5; \quad t=73.2; \quad t'=52.0; \quad a=0.0025387.$$

	Quantities used.	Vol. analysis.
Iodine	43.41	43.37
Iodide of potassium	56.59	56.63
	<hr/> 100.00	<hr/> 100.00

2. *Determination of Chlorine.*—Chlorine decomposes a solution of iodide of potassium instantly and completely, even in the cold, setting free an equivalent quantity of iodine. If this quantity be volumetrically determined in the manner just described, the quantity of chlorine will be given in the equation—

$$x = \frac{\text{Cl}}{\text{I}} a (nt - t'),$$

or in percentages, if the quantity used in the experiment was A :

$$x = \frac{100 \text{ Cl}}{A \cdot \text{I}} a (nt - t').^*$$

If, again, $A = \frac{100 \text{ Cl}}{\text{I}} a$, the difference of the two measurements $nt - t'$, will give at once the quantity of chlorine in 100 parts.

To give an idea of the great accuracy of this method, we may adduce an example of the determination of the density of chlorine. A stream of chlorine gas evolved from hydrochloric acid and peroxide of manganese, washed with water and dried by passing over chloride of calcium, was made to pass through a glass tube of the capacity of 91.005 cubic centimetres, drawn out at both ends, and connected with the gas-generating apparatus by means of a tube of vulcanised caoutchouc. As soon as the tube had assumed the constant temperature 2.1°C ., and the air had been completely expelled by the chlorine, the tube was tightly closed on the side next the generator by pressing the caoutchouc tube with the finger close to the aperture; and the other extremity, which remained open, dipped into a solution of iodide of potassium. Rapid absorption took place, the tube becoming completely filled with the liquid, which was at the same time decomposed, with separation of iodine. This liquid gave by the volumetric method above described: $n=9$; $t=44.7$; $t'=5.0$; $a=0.0025387$. From these elements it was found that the tube, which contained 91.005 cubic centimetres of water at 4°C ., contained 0.28191 grm. of chlorine at 0.7457 met. bar. and 2.1°C .; and this gives for the sp. gr. of chlorine—

Found.	Calculated.
2.4482	2.4489

3. *Determination of Bromine.*—A solution of bromine may be readily estimated in the same manner as chlorine, the result being calculated by the formula—

$$x = \frac{100 \text{ Br}}{\text{AI}} a (nt - t').$$

As commercial bromine always contains a little chlorine, which is very difficult to separate, the bromine used for testing the method was prepared from pure bromide of potassium. For this purpose 0.2869 grm. pure bichromate of potash was mixed with 2 or 3 grm. bromide of potassium, and distilled with concentrated hydrochloric acid from a small glass flask, and the bromine which passed over was received in a solution of iodide of potassium containing 0.9030 grm. of the iodide. As 1 at. $\text{K}_2\text{Cr}_2\text{O}_7$ liberates exactly 3 at. bromine, the bromine distilled off from the above mixture should weigh 0.4629 grm. The volumetric analysis gave the following results—

$$n=6; t=55.4; t'=44.4; A=1.3659; a=0.0025387;$$

whence :

	Used.	Found.
Iodide of potassium .	66.11	66.20
Bromine	33.89	33.80
	<hr/> 100.00	<hr/> 100.00

4. *Determination of Chlorine and Iodine together.*—When a mixture or compound of x chlorine and y iodine is to be determined, it is best to measure out two equal volumes of the liquid which contains them. One of these measures is mixed with sulphurous acid, till it loses its colour, and then precipitated with nitrate of silver. Let the weight of the precipitate of bromide and iodide of silver, collected on a filter after digestion for some time with dilute nitric acid, be A . The quantity of iodine $a (nt - t')$ equivalent to the chlorine and iodine together in the second measure is then determined by the method above given for bromine. These experiments give the following equations of condition—

$$\frac{\text{Ag} + \text{Cl}}{\text{Cl}} x + \frac{\text{Ag} + \text{I}}{\text{I}} y = A;$$

$$\frac{\text{I}}{\text{Cl}} x + y = a (nt - t')$$

whence :

$$x = \frac{A - \frac{\text{Ag} + \text{I}}{\text{I}} a (nt - t')}{\frac{\text{Ag} + \text{Cl}}{\text{Cl}} - \frac{\text{Ag} + \text{I}}{\text{I}}}$$

This method becomes inapplicable when the liquid contains hydrochloric acid and other compounds of chlorine. But as this condition is rarely fulfilled in practice, it is generally better to determine the iodine in one portion of the liquid as iodide of palladium. If the weight of the palladium obtained by igniting the precipitated iodide of palladium be π , the first of the two equations of condition takes the form, $\frac{I}{Pd} \pi = y$; whence

$$x = \frac{Cl}{I} a (nt - t') - \frac{Cl}{Pd} \pi.$$

An analysis of a sample of protochloride of iodine prepared with aqua-regia, gave—

$$\pi = 0.1156; t = 241.6; t' = 131.4; n = 1; a = 0.0050.$$

	Calculated.	Found.
Iodine	21.85	21.85
Chlorine	78.15	78.15
	<hr/> 100.00	<hr/> 100.00

5. *Determination of Chlorine and Bromine together.*—To estimate the quantity of chlorine contained in a sample of bromine, a quantity A of the bromine thoroughly dried is dissolved in solution of iodide of potassium, and the quantity of iodine, $a (nt - t')$, thereby separated, determined as above. The equations of condition, which form the basis of the calculation, and in which chlorine is denoted by y , and bromine by x , are—

$$x + y = A$$

$$\frac{I}{Br} x + \frac{I}{Cl} y = a (nt - t')$$

whence we find

$$y = \frac{a (nt - t') - \frac{I}{Br} A}{\frac{I}{Cl} - \frac{I}{Br}}$$

To test this method, 0.1148 grm. of bromine free from iodine and dried on chloride of calcium, was weighed in a glass bulb, converted by sulphurous acid into hydrobromic acid, and precipitated by nitrate of silver. The resulting chloride and bromide of silver weighed 0.2826 grm. Putting $0.1148 = A'$ and $0.2826 = B'$, the quantity of chlorine in the sample examined is found from the equations—

$$x + y = A'.$$

$$\frac{\text{Ag} + \text{Br}}{\text{Br}} x + \frac{\text{Ag} + \text{Cl}}{\text{Cl}} y = B'.$$

therefore

$$y = \frac{\frac{\text{Ag} + \text{Br}}{\text{Br}} A' - B'}{\frac{\text{Ag} + \text{Br}}{\text{Br}} - \frac{\text{Ag} + \text{Cl}}{\text{Cl}}}.$$

0.0948 grm. of the same bromine dissolved in iodide of potassium, gave by volumetric analysis—

$$A = 0.0948; n = 1; t = 80.5; t' = 17.3; a = 0.002578.$$

	Weighed analysis.	Vol. analysis.
Bromine . . .	93.42	93.34
Chlorine . . .	6.58	6.66
	<hr/> 100.00	<hr/> 100.00

6. *Determination of Chlorites and Hypochlorites.*—A solution of the salt is mixed with solution of iodide of potassium, and hydrochloric acid added till a slight acid reaction is produced. By means of the quantity of iodine $a(nt-t')$ separated in the solution, and determined by the volumetric method, the weight of chlorous acid x , or of hypochlorous acid x' , is found from the following equations, in which A denotes the weight of the salt or mixture of salts employed :

$$x = \frac{100 \ddot{\text{Cl}}}{4 \text{IA}} a (nt - t')$$

$$x' = \frac{100 \dot{\text{Cl}}}{2 \text{IA}} a (nt - t')$$

The method was tested upon a mixture of caustic potash and hypochlorite of potash. To obtain a perfectly definite quantity of the latter, 0.3256 grammes of pure bichromate of potash was boiled with fuming hydrochloric acid, and the chlorine, which passed over with the vapours of hydrochloric acid, conducted into a solution of 4 grammes of caustic potash. Now since 2 at. $\ddot{\text{K}} \ddot{\text{Cr}}_2$ eliminate under these circumstances exactly 3 at. $\dot{\text{Cl}}$, the potash-solution must absorb 0.1427 grammes of that substance. The volumetric analysis gave $n=4$; $t=83.6$; $t'=8$; $a=0.002578$, which corresponds with the following composition :

	Used.	Vol. analysis.
Aqueous potash	96.55	96.52
Hypochlorite of potash . .	3.45	3.48
	<hr/> 100.00	<hr/> 100.00

This method is peculiarly well adapted to the technical estimation of chloride of lime. If we take a solution of that substance containing $\frac{100 \text{ Cl}}{I}a$ of dry chloride of lime, the difference of the two measurements ($nt - t'$) gives directly the bleaching power of the product in per centages of chlorine.

7. *Determination of Sulphurous Acid and Sulphuretted Hydrogen.*—It has already been observed (p. 219), that sulphurous acid (and we may add sulphuretted hydrogen) cannot be exactly estimated by means of iodine, if the quantity of it contained in an aqueous solution exceeds 0.04 per cent. If, therefore, a more concentrated acid is to be examined, it must be diluted with boiled water till the total volume P has attained the required concentration. From this solution, p cubic centimetres are then measured off, starch added, and the quantity of iodine at determined which is required for the complete decomposition of the sulphurous acid. The quantity of anhydrous sulphurous acid contained in the volume P of the liquid is then given by the following equation—

$$x = \frac{P \ddot{S}}{p I} at.$$

The estimation of sulphuretted hydrogen is made in exactly the same manner, by means of the corresponding formula—

$$x' = \frac{P \dot{H}}{p I} at.$$

But the great facility with which sulphuretted hydrogen decomposes often renders this latter estimation very inexact.

A determination of the density of sulphurous acid gas made in a manner similar to that described for chlorine (p. 223),—excepting that the tube containing the gas dipped into boiled water, instead of a solution of iodide of potassium,—gave the following results:—

Volume of sulphurous acid gas at 1.1°C. , and $0.7507 \text{ met. bar.} = 90.699 \text{ cub. cent.}$

$$P = 1000; p = 194.0; t = 76.95; a = 0.0025387.$$

These numbers give for the density of the gas 2.190 ; the calculated density is 2.211 .

8. *Estimation of Chromates.*—When a chromate, *e. g.* bichromate

of potash, is boiled with excess of fuming hydrochloric acid, every 2 at. chromic acid eliminate 3 at. chlorine. The decomposition is rapid and complete. The 3 at. chlorine passed into a solution of iodide of potassium set free an equal number of atoms of iodine. If, therefore, we determine the quantity of $a (nt-l')$ obtained by using a known weight A of bichromate of potash, the quantity of chromic acid x contained in a quantity A of salt is found from the equation—

$$x = \frac{2 \ddot{\text{Cr}}}{3 \text{I}} a (nt-l')$$

or in 100 parts :

$$x' = \frac{200 \ddot{\text{Cr}}}{A \cdot 3 \text{I}} a (nt-l')$$

If again $A = \frac{200 \ddot{\text{Cr}}}{3 \text{I}} a$,—i.e. if the sample taken weighs exactly this quantity, then the difference of the two measurements $(nt-l')$ gives directly the percentage of chromic acid. Similarly for

$A = 100 \left(\frac{\ddot{\text{K}} + 2 \ddot{\text{Cr}}}{3 \text{I}} \right) a$, this difference would give the per-centage of neutral chromate of potash, and for $A = 200 \left(\frac{\ddot{\text{Pb}} + \ddot{\text{Cr}}}{3 \text{I}} \right) a$, the per-centage of pure chromate of lead in these respective salts.

The analysis is made by introducing a weighed quantity of the chromate into a small flask of the capacity of 36 to 40 cubic centimetres, filled about two-thirds with fuming hydrochloric acid, and having a gas-delivery tube adapted to the neck by means of a tube of vulcanised caoutchouc. Into the open extremity of this tube is inserted a small glass bulb with a narrow neck, which serves as a valve, and the tube is inserted into the neck of an inverted retort of the capacity of 160 cubic centimetres, and containing a solution of iodide of potassium. The middle of the neck of the retort is blown out into a bulb to receive any liquid that may be thrown up by the disengagement of gas. Instead of the glass bulb above mentioned, an excellent valve may be made by tying a piece of vulcanised caoutchouc tightly over the open end of the tube, and cutting a small slit in it, with a sharp, wet penknife. This slit opens when pressed from within, but closes tightly when pressed in the opposite direction. The liquid in the flask is now boiled for three or four minutes, by which time the whole of the chlorine is expelled, and liberates an equivalent quantity of iodine, which is estimated in the ordinary way.

0.7116 grm. pure bichromate of potash heated to the melting point gave off 0.0016 grm. water; and 1.0230 grm. reduced with

hydrochloric acid, and precipitated by continued digestion with ammonia, yielded 0.5327 grm. of ignited sesquioxide of chromium.

The volumetric analysis gave—

$$A=0.2379; n=3; t=5; t'=81.6; a=0.0025387;$$

and in another experiment—

$$A=0.2943; n=3; t=103.7; t'=16.0; a=0.0025387.$$

This gives—

Weighed analysis.		Volumetric analysis.	
		I.	II.
Chromic acid . . .	68.18	68.32	67.95
Potash	31.60	31.47	31.83
Water	0.22	0.22	0.22
<hr/>		<hr/>	<hr/>
100.00		100.00	100.00

Another sample, composed of 0.4632 grm. chromate of potash dried at 150° C., and 1.27 grm. sulphate of potash, gave—

$$A=1.7332; t=101.7; t'=38.2; n=5; a=0.0025387.$$

	Taken.	Vol. analysis.
Chromate of potash . .	26.72	26.91
Sulphate of potash . .	73.28	73.09
<hr/>		<hr/>
100.00		100.00

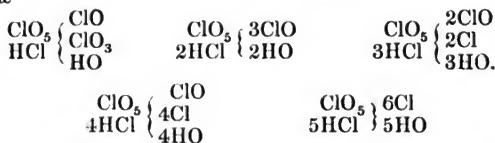
The volumetric analysis of pure bichromate of potash gives, as above observed (p. 221), the simplest method of determining the value of a , or the quantity of pure iodine corresponding to the weight of impure iodine contained in a degree of the burette. This value is obtained from the equation—

$$a = \frac{3 I A}{(\dot{K} + 2 \ddot{C}r) (nt - t')}$$

The action of concentrated hydrochloric acid on chromates often gives rise to the formation of traces of volatile chromate of terchloride of chromium, $\text{CrCl}_3 \cdot 2\text{CrO}_3$. This, however, does not affect the result of the analysis, inasmuch as the quantities of chlorine, chromic acid, and terchloride of chromium, obtained from a given weight of a chromate, eliminate the same quantity of iodine.

9. *Estimation of Chlorates.*—The action of hot concentrated hydrochloric acid on chlorates is well known to be attended with a reduction of the chloric acid. The reaction, which is not attended

with any evolution of oxygen, may be expressed by one of the following formulæ—



It is impossible to determine by theory which of these reactions actually takes place, or which of them may occur simultaneously. But this uncertainty is of no importance, for, whatever may be the reaction which takes place, when the products are brought in contact with the iodide of potassium, 6 at. iodine are set free for each atom of hydrochloric acid. Consequently, x parts of a chlorate $\text{R} \overset{\cdot\cdot\cdot}{\text{Cl}}$ decomposed by hydrochloric acid liberate $\frac{6 \text{ I}}{\text{R} \overset{\cdot\cdot\cdot}{\text{Cl}}} x$. This iodine $a (nt - t')$ estimated by the volumetric method, gives for the value of x —

$$x = \frac{\text{R} \overset{\cdot\cdot\cdot}{\text{Cl}}}{6 \text{ I}} a (nt - t')$$

Similarly the per-centage of chloric acid contained in a quantity A of a chlorate is determined by the equation—

$$x' = \frac{100 \overset{\cdot\cdot\cdot}{\text{Cl}}}{A \cdot 6 \text{ I}} a (nt - t')$$

and if A be taken $= \frac{100 \overset{\cdot\cdot\cdot}{\text{Cl}}}{6 \text{ I}} a$, the difference $a (nt - t')$ gives immediately the per-centage of chloric acid.

An experiment with pure chlorate of potash gave—

$A = 0.0889$; $n = 3$; $t = 74.1$; $t' = 7.2$; $a = 0.002578$.

Calculated.		Found.
Chloric acid	. . . 61.57	61.83
Potash	. . . 38.43	38.17
	<hr/> 100.00	<hr/> 100.00

10. *Estimation of the Peroxides of Lead, Manganese, Nickel, Cobalt, &c.*—The percentage of oxygen in peroxide of lead is given by the formula—

$$x = 100 \frac{2 \text{ O}}{A \cdot \text{I}} a (nt - t')$$

A sample of the peroxide which was prepared by boiling red lead with acetic acid, and yielded by ignition in a stream of dry air, 0.004 grm. water, and 0.043 grm. oxygen, gave by volumetric analysis on 0.7402 grm., $n=5$; $t=58.8$; $t'=9.8$; $a=0.002578$. Hence—

	Calculated.	Weighed analysis.	Vol. analysis.
Lead . .	86.12	87.23	86.95
Oxygen .	13.31	12.20	12.48
Water .	0.57	0.57	0.57
	<hr/> 100.00	<hr/> 100.00	<hr/> 100.00

The per-centage of peroxide of manganese in a sample of commercial black oxide A is given by the formula—

$$x = \frac{100 \text{ Mn}}{A \cdot I} a (nt - t')$$

0.4839 grm. manganoso-manganic oxide, obtained by igniting pure carbonate of manganese, gave—

$$A=0.4839; n=3; t=78.3; t'=16.4; a=0.0025387.$$

A second analysis of the same product gave—

$$A=0.3725; n=3; t=75.7; t'=59.4; a=0.0025387.$$

	Calculated.	Volumetric analysis.	
		I.	II.
1 at. MnO_2 . .	37.98	39.37	39.25
2 at. MnO . .	62.02	60.63	60.75
	<hr/> 100.00	<hr/> 100.00	<hr/> 100.00

It would appear from these two experiments that the degree of oxidation which manganese acquires by the ignition of its oxides does not agree exactly with the formula usually assigned to it. If this is the case, the error thence arising in estimations of manganese may be easily corrected by a volumetric analysis of the ignited precipitate.

A pyrolusite from Bohemia, which, according to a weighed analysis, contained 0.32 per cent. silica, 0.08 per cent. ferric oxide, and 0.5 per cent. water, gave—

$$A=0.3128; n=5; t=79.3; t'=44.0; a=0.0025387.$$

Peroxide of manganese	98.25
Sesquioxide of iron	0.08
Silica	0.32
Water	0.50
	<hr/> 99.15

In presence of lime, magnesia, oxide of zinc, and similar strong bases, the oxides of manganese yield, by ignition in the air, not $\text{MnO} \cdot \text{Mn}_2\text{O}_3$, but, when lime or magnesia is present, $\left. \begin{matrix} \text{MnO} \\ \text{MgO} \end{matrix} \right\} \text{Mn}_2\text{O}_3$, or if magnesia is in excess, $\text{MgO} \cdot \text{Mn}_2\text{O}_3$. If, therefore, we wish to determine, not merely the quantity of separable oxygen in the peroxides of manganese, but likewise the quantity of metallic manganese, this circumstance must be taken into consideration.

11. *Estimation of Iodic, Vanadic, Selenic, Manganic, Ferric Acid, Ozone, &c.*—As all these and many other volumetric determinations may be made by one and the same method, and the corresponding equation of condition is easily deduced from the principles above explained, it will be sufficient to give a single example, viz. that of the determination of iodic acid.

When iodic acid, either free or combined with a base, is distilled with excess of fuming hydrochloric acid, each atom of iodic acid eliminates 4 atoms of chlorine, while 1 atom of protochloride of iodine remains in the liquid. The percentage of iodic acid in a mixture of salts whose weight is A , is therefore determined according to the process described for the estimation of chlorine by means of the equations—

$$x = \frac{100 (\ddot{\text{R}} + \ddot{\text{I}})}{A \cdot 4\text{I.}} a (nt - t')$$

A mixture of 0.5321 chloride of calcium with 0.2755 iodate of baryta gave—

$$n=3; \quad t=85.5; \quad t'=31.4; \quad a=0.002578.$$

	Used.	Vol. analysis.
Chloride of calcium . .	65.53	65.89
Iodate of baryta . . .	34.47	34.11
	<hr/> 100.00	<hr/> 100.00

12. *Volumetric Separation of Cerium and Lanthanum.*—These metals are precipitated together as oxides, the precipitate dissolved in strong sulphuric acid, and the solution precipitated by potash. The precipitate, consisting of the hydrated protoxides of the two metals, is suspended in a strong solution of potash, a stream of chlorine passed through the liquid, and the precipitate carefully washed with cold water. The precipitate consisting of ceroso-ceric oxide is treated while still moist with fuming hydrochloric acid (in the flask above described, p. 228), in which it dissolves with brown colour. On heating the mixture, each atom of ceroso-ceric oxide eliminates 1 atom chlorine, which separates 1 atom iodine from the iodide of potassium

in the retort. If this quantity of iodine is $a (nt-t')$, then the quantity of the ceroso-ceric oxide contained in the precipitate is—

$$x = \frac{3 \text{ Ce} + 4 \text{ O}}{\text{I}} a (nt-t')$$

or, expressed as cerous oxide—

$$x' = \frac{3 \text{ Ce}}{\text{I}} a (nt-t')$$

A mixture of cerous and lanthanous oxides carefully purified from all other metals, was treated seven times with potash and chlorine as above, and the yellow precipitate dried up to a moist jelly. An indefinite quantity of this precipitate gave by volumetric analysis—

$$n=2; \quad t'=20.1; \quad t=106.9; \quad a=0.0025387.$$

The solution of cerous oxide remaining in the flask gave by precipitation with oxalate of ammonia after neutralisation, 1.2127 grm. oxalate of cerium: 0.5275 grm. of this precipitate burned with oxide of copper gave 0.2073 grm. carbonic acid and 0.0460 water. Assuming that the salt is neutral, the quantity of oxygen in the cerous oxide must be one-third of that in the oxalic acid, and, therefore, the composition of cerous oxide must be—

Cerium	87.918
Oxygen	12.082
					100.000

Hence the atomic weight of cerium must be 727.7 (O=100) or 58.22 (H=1). Assuming this to be correct, we obtain—

	Calculation.	Analysis.
1 at. cerous oxide . . .	59.45	59.13
1 at. oxalic acid . . .	32.47	32.15
1 at. water . . .	8.08	8.72
		100.00
		100.00

According to these numbers, the cerous oxide in the entire quantity of oxalate 1.2137, must contain 0.0866 oxygen. Before the reduction with hydrochloric acid, the cerium was associated with another portion of oxygen, which, by means of the above formula and volumetric data, is found to be 0.0296. Now, 0.0866 : 0.0296 :: 3 : 1. Thus :

	Found.	Calculated.
Oxygen in cerous oxide	0.0866	0.0872
Excess of oxygen in ceroso-ceric oxide	0.0296	0.0291

Hence we may conclude, that hydrated cerous oxide, when treated with chlorine in a solution of caustic potash, is converted into a higher oxide of the form $\text{CeO} \cdot \text{Ce}_2\text{O}_3$, and that the behaviour of this latter oxide when heated with hydrochloric acid, may be applied to the volumetric estimation of cerium, even in presence of lanthanum. It remains, however, to be determined whether cerous oxide in presence of lanthanous oxide may not be converted by hypochlorous acid into $\text{LaO} \cdot \text{Ce}_2\text{O}_3$.

Besides the preceding and a great number of other bodies which give rise to a separation of free chlorine, the volumetric method above described may likewise be applied to the estimation of those substances which are easily and completely raised by chlorine to a higher degree of oxidation. These substances are heated with fuming hydrochloric acid and a weighed quantity of pure bichromate of potash, the evolved chlorine passed into a solution of iodide of potassium, and the separated iodine estimated as above. The quantity thus separated, viz.,

a ($nt=t'$) is equal to the quantity of iodine $\frac{p \cdot 3 \text{I}}{\dot{\text{K}} \ddot{\text{Cr}}_2}$, equivalent to

the chromate of potash used, *minus* the quantity i , equivalent to the protoxide employed. The latter is therefore—

$$i = \frac{p \cdot 3 \text{I}}{\dot{\text{K}} + 2\ddot{\text{Cr}}} - a(nt-t')$$

Hence the weight of the substance itself may be easily calculated, as in the following examples.

13. *Estimation of Ferrous Oxide alone and in conjunction with Ferric Oxide.*—The quantity of ferrous oxide b in a sample of iron ore, &c., may be found from the following considerations: i denotes the quantity of iodine which the ferrous oxide subjected to volumetric examination requires in order to convert it into ferric oxide. Now this quantity of iodine is to the ferrous oxide present as $\text{I} : 2\ddot{\text{Fe}}$. Hence, substituting for i its value above given, we find for the quantity of ferrous oxide in the compound examined—

$$(1) \quad e = \frac{6 \ddot{\text{Fe}}}{\dot{\text{K}} + 2\ddot{\text{Cr}}} p - \frac{2 \ddot{\text{Fe}}}{\text{I}} a(nt-t');$$

the corresponding quantity of iron is—

$$(2) \quad e' = \frac{6 \text{Fe}}{\dot{\text{K}} + 2\ddot{\text{Cr}}} p - \frac{2 \text{Fe}}{\text{I}} a(nt-t')$$

and the equivalent quantity of ferric oxide—

$$(3) \quad e'' = \frac{3 \ddot{\text{Fe}}}{\ddot{\text{K}} + 2 \ddot{\text{Cr}}} p - \frac{\ddot{\text{Fe}}}{\text{I}} a (nt - t').$$

The formula (1) is true only so long as the equation of indication $\frac{\text{I}}{2 \ddot{\text{Fe}}} < \frac{3 \text{I}'}{\ddot{\text{K}} + 2 \ddot{\text{Cr}}}$ is satisfied. This is the case when one or more

parts by weight of bichromate of potash are used for every 1 part by weight of the iron-compound. The equations (2) and (3) are of course subject to corresponding limitations.

To estimate ferrous oxide, either by itself or in conjunction with ferric oxide, the flask (p. 228) is two-thirds filled with fuming hydrochloric acid, and the air in the upper part expelled by carbonic acid evolved by throwing a few grains of carbonate of soda into the acid. When all the air has thus been expelled, the chromate of potash p and the substance A , weighed in a small open glass tube, are thrown into the acid, the gas-delivery tube put on, and the process conducted as for the estimation of chromates.

Magnetic iron ore from the Tyrol, crystallised in beautiful octohedrons, gave by this method, after thorough drying—

$$A = 0.2869; \quad p = 0.4206; \quad n = 6; \quad t = 71.3; \quad t' = 65.6; \\ a = 0.0025387.$$

	Calculation.	Analysis.
1 at. Fe_2O_3	68.97	68.96
1 at. FeO	31.03	31.04
	<hr/> 100.00	<hr/> 100.00

To determine metallic iron or ferric oxide, the substance is dissolved in hydrochloric acid, and the sesquioxide of iron completely reduced to protoxide by boiling with sulphurous acid, or better with chemically pure zinc. The ferrous solution is then treated with hydrochloric acid and bichromate of potash as above.

0.5603 grm. of fine bright harpsichord-wire was dissolved in aqua regia: the silica removed by evaporation and re-solution in acid, and the ferric oxide precipitated by ammonia; it weighed after ignition 0.7977 grm.

0.2087 grm. of the same wire gave by the volumetric method—

$$A = 0.2087; \quad n = 1; \quad t = 68.4; \quad t' = 11.0; \quad a = 0.0025387.$$

	Quantities used.	Volumetric analysis.
Iron	99.66	99.62
Carbon and silicum	0.34	0.38
	<hr/> 100.00	<hr/> 100.00

14. *Estimation of Arsenious Acid and its Salts.*—If A be the weight of the substance containing the arsenious acid, and p the quantity of bichromate of potash acid, the percentage of arsenious acid is given by the equation—

$$x = \frac{100}{A} \left[\frac{3 \ddot{\text{As}}}{2(\ddot{\text{K}} + 2\ddot{\text{Cr}})} p - \frac{\ddot{\text{As}}}{2 \text{I}} a (nt - t') \right].$$

The quantity of iodine consumed by the arsenious acid x in the substance A is $\frac{2 \text{I}}{\ddot{\text{As}}} x$, and the iodine set free by p is $\frac{2 \text{I}}{\ddot{\text{K}} + 2\ddot{\text{Cr}}} p$.

The weight of the arsenical substance must therefore be so proportioned to the bichromate of potash that the equation of condition, $\frac{2 \text{I}}{\ddot{\text{As}}} x < \frac{3 \text{I}}{\ddot{\text{K}} + 2\ddot{\text{Cr}}} p$, may be satisfied: that is to say, that there may always be more than 0.998 parts of bichromate of potash to 1 part of the arsenical substance.

0.2615 grm. of pure arsenious acid mixed with 0.5274 grm. gypsum, and treated as above with 0.4334 grm. bichromate of potash, gave—

$$A = 0.7889; p = 0.4334; n = 3; t = 79.8; t' = 66.4; \\ a = 0.0025387.$$

	Quantities used.	Volumetric analysis.
Arsenious acid	33.15	33.14
Gypsum	66.85	66.86
	<hr/> 100.00	<hr/> 100.00

Researches on Oxygen in the Nascent State.*

By A. Housseau.

WHEN peroxide of barium is acted upon at ordinary temperatures by monohydrated sulphuric acid, the oxygen evolved possesses very active oxidising properties. A simple apparatus for the purpose consists of a tubulated flask, to the narrower neck of which is adapted a tube to convey the gas into a jar standing over water. The sulphuric acid being first poured into the flask, the peroxide of barium is added to it in small fragments, and the neck quickly closed with a cork. The disengagement of gas soon begins, and is more rapid as the acid mixture becomes more strongly heated. It is therefore sometimes necessary to accelerate the action by immersing the flask in a water-bath;—at other times, on the contrary, to moderate it by the use of cold water.

Nascent oxygen is a colourless gas having a powerful odour; it must be respired with caution, for if introduced into the system in large quantity, it gives rise to nausea, which may be followed by vomiting. Its odour also, which at first is by no means unpleasant, becomes insupportable after smelling it frequently: its taste resembles that of the lobster.

When heated to 75° C. (168° F.), or exposed to the sun's rays, it loses all its active properties. In presence of water, and at ordinary temperatures, it oxidises most of the metals,—even silver,—peroxidises metallic protoxides, and immediately transforms arsenious into arsenic acid, &c. The alkalis (potash, soda, lime, baryta), and the stronger acids (sulphuric, phosphoric, nitric), act powerfully on it.

Ammonia in contact with nascent oxygen undergoes a true combustion, the product of which is a nitrous compound: on plunging a glass rod, dipped in ammonia, into a jar of the odoriferous oxygen, the vessel is immediately filled with white fumes of nitrate of ammonia.

Phosphuretted hydrogen of the non-spontaneously inflammable variety, which is not acted upon at 20° C. (58° F.) by ordinary oxygen, burns with emission of light in the odoriferous gas.

Lastly, hydrochloric acid, dissolved in water, is completely decomposed by nascent oxygen; the hydrogen is burned, and the liberated chlorine dissolves gold-leaf immersed in the modified acid.

Nascent oxygen is, therefore, a chlorinising agent, in the same manner as chlorine is an oxidising agent: it is, in fact, to this remarkable power of combustion in nascent oxygen that the metallic peroxides owe their faculty of eliminating chlorine under the influence of hydrochloric acid.

* Compt. rend. xl. 947.

The odoriferous gas acts still more rapidly on iodide of potassium, liberating the iodine; it decolourises spontaneously the tinctures of litmus, cochineal, campeachy wood, sulphate of indigo, &c., exhibiting a bleaching power equal to that of chlorine itself. Porous bodies absorb nascent oxygen, and modify it in a remarkable manner; for when the gas is slowly passed through a glass tube filled with asbestos, platinum-black, lint, carded cotton, shreds of flannel, &c., its odour and oxidising properties are completely destroyed.

The following table gives a summary of the differences between ordinary and nascent oxygen :—

<i>Properties of ordinary oxygen in the free state, and at the temperature of 15° C. (60° F.)</i>	<i>Properties of nascent oxygen in the free state, and at the temperature of 15° C. (60° F.)</i>
Colourless gas, inodorous and tasteless.	Colourless gas, having a very powerful odour, and the taste of lobsters.
Has no action on blue litmus.	Rapidly decolourises blue litmus.
Does not oxidise silver.	Oxidises silver.
Has no action on ammonia.	Burns ammonia spontaneously, and transforms it into nitrate.
Has no action on phosphuretted hydrogen.	Instantly burns phosphuretted hydrogen, with emission of light.
Does not decompose iodide of potassium.	Acts rapidly on iodide of potassium, setting the iodine free.
Has no action on hydrochloric acid.	Decomposes hydrochloric acid, setting the chlorine free.
Has a feeble oxidising action.	Is a powerful oxidising and chlorinising agent.
Very stable at all temperatures.	Stable at 15° C., but destroyed towards 75°.

Peroxide of barium is not the only body which is capable of yielding active oxygen. Oxygen in the combined state possesses, indeed, the intensified power which distinguishes free oxygen in the nascent state, and which it ceases to exhibit when completely isolated, because the temperature at which it is usually evolved from its combinations is equal or superior to that at which active oxygen passes into the ordinary state.

[It appears from the experiments of Dr. Andrews, lately communicated to the Royal Society,* that *ozone*, evolved by the electrolysis of water, and stated by Baumert† and others to be a peroxide of hydrogen, is nothing but active oxygen. Andrews attributes the results obtained by these chemists to the presence of a small quantity of carbonic acid, which always accompanies electrolytic oxygen, and

* Proc. Roy. Soc. vii. 475.

† Chem. Soc. Qu. J. vi. 169.

is difficult to remove. He also confirms the statement of Frémy and Becquerel, that ozone is formed by the action of the electric spark on perfectly pure and dry oxygen; and shows that ozone, however prepared, has always the same properties, and is not a compound body, but oxygen in an altered or allotropic condition.—ED.]

On Aluminium.*

By H. Ste.-Claire Deville.

ALUMINIUM was discovered, in 1827, by Wöhler,† who obtained it by reducing the chloride with potassium in the form of a grey powder; and afterwards showed‡ that by the same method the metal may be obtained in fused globules. He described it as a tin-white, perfectly malleable metal, which does not tarnish by exposure to the air; melts in the blowpipe flame; has a density of 2.5, increasing by hammering to 2.67; not decomposing water at ordinary temperatures, but evolving hydrogen from it slowly at 100° C.

Devil has lately obtained the metal in much larger quantities, and has studied its properties more minutely. He prepares it by two methods:—1, by reducing the chloride of aluminium with sodium; 2, by reducing the double chloride of aluminium and sodium by electrolysis.

To prepare the chloride of aluminium, Deville mixes ignited alumina with charcoal and oil, to the consistence of a paste; heats the mixture in a crucible; introduces the pulverised mass into a tubulated earthen retort, having a short neck to which a bell-shaped receiver is adapted; heats the retort to dull redness; and then passes chlorine gas into it: chloride of aluminium then passes over after a short time.

To decompose the chloride of aluminium with sodium,§ 200 or 300 grammes of the chloride are placed in a wide glass tube between two plugs of asbestos; pure dry hydrogen passed through the tube; and the chloride of aluminium heated (the stream of hydrogen being continued) to drive out hydrochloric acid, chloride of sulphur, and chloride of silicium, which are formed at the same time. A number of porcelain boats, each containing a few grammes of sodium dried between bibulous paper, are then introduced into the tube; and the

* Ann. Ch. Phys. [3], xliii. 5.

† Pogg. Ann. xi. 146.

‡ Ann. Ch. Pharm. liii. 422.

§ For the preparation of sodium, Deville recommends a mixture of 717 parts dry carbonate of soda, 175 charcoal, and 108 chalk,—the latter for the purpose of keeping the mixture during the heating in a pasty condition, and to condense the sodium in a small receiver, as recommended by Maresca and Donny (Ann. Ch. Phys. [3], xxxv. 147).

tube is heated till the sodium melts and the chloride of aluminium volatilises in the atmosphere of hydrogen, and, coming in contact with the sodium, is thereby decomposed. As soon as all the sodium has disappeared, and the resulting chloride of sodium has taken up chloride of aluminium to saturation, the porcelain boats are withdrawn from the glass tube, and introduced into a wide porcelain tube, in which they are heated in a stream of pure hydrogen till the double chloride of sodium and aluminium volatilises and condenses in the receiver. The aluminium which remains behind, aggregated in one or two masses, is washed out with a little water, to remove small quantities of the double salt and of brown silicium (produced by the action of sodium and aluminium on the silica in the porcelain). To unite the separate globules of aluminium into one, a quantity of chloride of aluminium and sodium is then fused in a porcelain crucible; the aluminium added to it as soon as the evolution of hydrochloric acid (proceeding from adhering moisture) ceases; the heat increased till the aluminium fuses together; the excess of the double chloride poured off after the metal has solidified by cooling; and the aluminium kept in a state of fusion in a covered porcelain crucible, till the adhering double chloride is completely volatilised. A globule of very pure aluminium is then found at the bottom of the crucible, coated with a thin pellicle of alumina proceeding from the partial decomposition of the flux.

Aluminium may also be reduced from the chloride by means of vapour of sodium. For this purpose, the sodium disengaged by heating a mixture of carbonate of soda, charcoal, and chalk, is made to pass into a large earthen crucible by means of an iron tube passing from the bottle containing the mixture through a hole in the side of the crucible. The oxide of carbon, which first passes into the crucible, burns at the bottom, heats and dries it; afterwards the vapour of sodium passes over; and, as soon as the flame of that metal becomes visible, chloride of aluminium is thrown into the crucible in small pieces from time to time, and is there reduced. At the end of the operation the crucible is broken, and the saline mass, composed of chloride of sodium, small globules of aluminium, and charcoal impregnated with soda, is digested in water if acid, in dilute nitric acid if alkaline, to dissolve out the saline matters. The several globules of aluminium are then fused into one in the manner already described. The author has not yet perfected this latter method; but it appears to promise very good results, yielding a considerable quantity of very pure aluminium even from very impure chloride.*

Electrolytic process.—The double chloride of aluminium and

* From a paper recently published by H. Rose (Pogg. Ann. xevi. 152), it appears that aluminium may be much more advantageously obtained by the action of sodium on *Cryolite*, which is a native fluoride of aluminium and sodium.

sodium, prepared by fusing in a porcelain crucible at 200° C. a mixture of 2 parts chloride of aluminium and 1 part dry and pulverised chloride of sodium, is introduced into a heated porcelain crucible, in the cover of which are two apertures,—one near the edge of the crucible, to admit a broad platinum plate, which forms the negative pole of the battery; and the other in the middle, to admit a porous cylindrical cell, likewise filled with the fused double chloride, in which is immersed a piece of dense charcoal, serving as the positive pole. On passing the current of a few galvanic elements through this arrangement, the aluminium separates, together with chloride of sodium, on the platinum plate, which must be taken out from time to time, quickly freed, when cold, from the deposit which has formed upon it, and again immersed: pieces of dry chloride of sodium must be dropped into the porous cell from time to time, to compensate for the quantity which passes to the negative pole. When the several deposits removed from the platinum plate are collected together, and fused in a crucible, and the fused mass treated with water, chloride of sodium dissolves, and a grey metallic powder remains, which, by repeated fusion with the chloride of aluminium and sodium, may be united into bright metallic masses.*

Properties of Aluminium.—Pure aluminium is white, with a faint bluish iridescence: when recently fused, it is soft, like pure silver, and has a density of 2.56; but, after hammering or rolling, it is as hard as iron, and has a density of 2.67. It conducts electricity eight times as well as iron, and is slightly magnetic. Its melting point is between that of zinc and that of silver; when solidified from fusion, and also when reduced by electrolysis, it exhibits crystalline forms (apparently regular octohedrons). It does not oxidise in the air, even at a strong red heat, neither does it decompose water, excepting at the strongest red heat,—and even then but slowly. It does not dissolve in nitric acid, either dilute or concentrated, at ordinary temperatures, and but very slowly in boiling nitric acid; dilute sulphuric acid scarcely attacks it at ordinary temperatures, even after a long time; hydrochloric acid, of any degree of concentration, dissolves it readily, even at low temperatures, with evolution of hydrogen. Sulphuretted hydrogen has no action upon it; neither is it attacked by the fused hydrates of the alkalis. It does not combine with mercury; and, when fused with lead, takes up only traces of that metal. With copper it unites in various proportions, forming light, very hard, and white alloys; and combines also with silver and iron. The aluminium obtained by Deville in the manner above described differs in

* Bunsen (Pogg. Ann. xcii. 648) has obtained aluminium in compact masses by a similar process,—the same, in fact, that he had previously applied to the reduction of magnesium (Ann. Ch. Pharm. lxxxii. 137).

some respects from Wöhler's aluminium,—chiefly in being less fusible, and in not decomposing water. Deville attributes the inferior fusibility of Wöhler's aluminium to the presence of platinum (proceeding from the platinum tube which Wöhler used to effect the decomposition); and its power of decomposing water to the presence of potassium or of undecomposed chloride of aluminium.

Devilie did not succeed in reducing aluminium by electrolysis from an aqueous solution of any of its compounds; but, according to G. Gore,* this metal may be reduced on copper by the galvanic current from a solution of hydrochlorate or acetate of alumina, or more slowly from a solution of alum; it then forms a lead-coloured deposit, which acquires the colour of platinum by polishing.

New Form of Silicium.—The first portions of aluminium obtained by Deville's electrolytic process contain silicium and other impurities derived from the chloride of aluminium used: one sample was found to contain 10·3 per cent. silicium, and 89·7 aluminium, with a trace of iron. On treating this impure and highly crystalline aluminium with hydrochloric acid, hydrogen gas having a very offensive odour is evolved, and silicium remains behind in the form of shining metallic laminæ, which may be heated to whiteness in a stream of oxygen without alteration, are not dissolved by any acid excepting a mixture of hydrofluoric and nitric acids, and are but very slowly oxidised by fused potash, even at a red heat. This modification of silicium, which appears to be related to the previously known forms of that substance, in the same manner as graphite to charcoal, is a conductor of electricity (Devilie).

ON GLUCINUM AND ITS COMPOUNDS.†

By H. Debray.

GLUCINA was discovered by Vauquelin in 1797 in the emerald of Limoges, and has since been found in cymophane; chrysoberyl, phenakite, the gadolinites, leucophane, and helvine; but, on account of the great difficulty of preparing it, its properties and the constitution of its compounds have not hitherto been satisfactorily studied. Berzelius, from the similarity of its behaviour in solution with that of alumina, and from its insolubility in acids after calcination, was

* Phil. Mag. [4], vii. 227.

† Ann. Ch. Phys. [3], xlv. 5.

led to regard it as a sesquioxide, Gl_2O_3 ,—a view which was further confirmed by the discovery of H. Rose, that chloride of glucinum may be prepared in the same manner as chloride of aluminum; and by the similarity of the metal (isolated by Wöhler in 1827) to metallic aluminum. But in 1843 Awdejew,* after having vainly endeavoured to obtain a sulphate of glucina and potash analogous to common alum, prepared one in which the potash and the glucina were combined with equal quantities of sulphuric acid,—agreeing, in fact, with the formula $\text{KO}, \text{SO}_3 + \text{GlO}, \text{SO}_3 + 2\text{HO}$; and likewise a double fluoride of similar constitution: $\text{KFl} + \text{GlFl}$. This view of the constitution of glucina was further confirmed by the examination of several minerals containing that earth,—particularly of the cymophanes from the Ural and from Ceylon, in which the relative quantities of glucina and alumina were found to be as constant as in the emerald,—contrary to the generally-received opinion, that glucina and alumina are capable of replacing one another as bodies of similar constitution. Regarding glucina as a protoxide, GlO , the formula of cymophane is $\text{GlO}, \text{Al}_2\text{O}_3$, and that of the emerald, $\text{GlOSiO}_3 + \text{Al}_2\text{O}_3, 3\text{SiO}_3$. The formulæ of all these compounds on the hypothesis of Berzelius are much more complicated. From the analysis of the sulphate of glucina regarded as GlO , Awdejew deduced for the metal the atomic weight 4.65 ($\text{H}=1$), which is less than that of any of the other elements except hydrogen. This circumstance was regarded by Berzelius as a capital objection to Awdejew's theory; and he accordingly (admitting the correctness of Awdejew's analysis) fixed the atomic weight of glucinum at 15.77, regarding glucina as Gl_2O_3 . It appears also from Ebelmen's researches on the artificial formation of minerals, that glucina crystallises in the same form as alumina. This circumstance cannot, however, be regarded as of much importance with reference to the formula of glucina, inasmuch as oxide of zinc, which is universally regarded as a protoxide, likewise crystallises in the same form as alumina.

The following researches were made with the view of supplying additional materials for the decision of this question, and contributing further to the knowledge of glucinum and its compounds.

The metal *Glucinum* is obtained from the chloride by reduction with sodium, in a manner similar to that adopted by Deville for the preparation of aluminium (page 239). It is a white metal, whose density is 2.1. It may be forged and rolled into sheets in the cold; its melting point is below that of silver. It may be melted in the outer blowpipe flame, without exhibiting the phenomenon of ignition presented by zinc and iron under the same circumstances; it cannot even be set on fire in an atmosphere of pure oxygen, but in both experiments becomes covered with a thin coat of oxide, which seems

* Ann. Ch. Phys. [3], vii. 155.

to protect it from further oxidation. It is not attacked by sulphur, even when melted in the vapour of that substance; and as Frémy did not succeed in obtaining a sulphide of glucinum by heating glucina with charcoal and sulphide of carbon, it seems probable that glucinum does not form a sulphide. Chlorine acts upon glucinum with the aid of a gentle heat, but without vivid incandescence, the metal merely becoming red-hot when exposed to a rapid current of chlorine. Iodine combines readily with glucinum at a dull red heat; at lower temperatures, part of the iodine remains in excess, and forms with the iodide of glucinum a reddish mass, which becomes liquid and blackish under the influence of a larger quantity of iodine. Silicium unites readily with glucinum, forming a hard brittle substance, susceptible of a high polish: this alloy is always obtained when glucinum is reduced in porcelain vessels. Glucinum does not decompose water at a boiling heat, or even when heated to whiteness. Gaseous hydrochloric acid attacks the metal at the temperature produced by a small spirit-lamp, the action being attended with evolution of heat. Aqueous hydrochloric acid, even when dilute, attacks it readily, with evolution of hydrogen; if the metal contains silicium, that substance remains behind in the graphite-like form first observed by Deville (page 242). Sulphuric acid, either dilute or concentrated, acts like hydrochloric acid. Nitric acid, even when concentrated, does not act upon glucinum at ordinary temperatures, and dissolves it but slowly even at a boiling heat. Glucinum is not attacked by ammonia, but dissolves readily in solution of potash. The above-mentioned properties differ considerably from those of the metal which Wöhler obtained by igniting chloride of glucinum with potassium in a platinum crucible, the metal thus obtained being a grey powder, very refractory in the fire, but combining with oxygen, sulphur, and chlorine, much more energetically than Debray's metal. The differences, however, appear to be due, partly to the difference of aggregation, and partly to the contamination of Wöhler's metal with platinum and potassium.

Glucina, $\text{GlO} = 4.54 + 8 = 12.54$.—Debray prepares this earth from the emerald of Limoges by the following process:—The mineral, finely pounded, is fused with half its weight of quicklime in an air furnace, and the glass thus obtained is treated, first with dilute, and then with strong nitric acid, till it is reduced to a homogeneous jelly. The product is then evaporated to dryness, and heated sufficiently to decompose the nitrates of alumina, glucina, and iron, and a small portion of the nitrate of lime; and the residue, consisting of silica, alumina, glucina, sesquioxide of iron, nitrate of lime, and a small quantity of free lime, is boiled with water containing sal-ammoniac, which dissolves the nitrate of lime immediately, and the free lime, after a while, with evolution of ammonia (if no ammonia is evolved,

the calcination has not been carried far enough, and must be repeated). The liquid is then decanted; the precipitate, after thorough washing, treated with boiling nitric acid; and the resulting solution of alumina, glucina, and iron, poured into a solution of carbonate of ammonia mixed with free ammonia. The earths are thereby precipitated without evolution of carbonic acid, and the glucina redissolves, after seven or eight days, in the excess of carbonate of ammonia. As the carbonate of ammonia may also dissolve a small quantity of iron, it should be mixed with a small quantity of sulphide of ammonium, to precipitate the iron completely. Lastly, the carbonate of ammonia is distilled off, and the carbonate of glucina which remains yields pure glucina by calcination.

Glucina is a white, loosely-coherent powder, without taste or smell. It is infusible even in a blowpipe flame fed with ether-vapour and oxygen, but volatilises at that temperature like magnesia and oxide of zinc. It is not hardened by heat, like alumina, but merely rendered less soluble in acids. Ebelmen has obtained it in hexagonal prisms, by exposing a solution of glucina in fused boracic acid to a powerful and long-continued heat. It may be more easily obtained in microscopic crystals, apparently of the same form, by decomposing the sulphate of glucina at a high temperature in presence of sulphate of potash; also by calcining the double carbonate of glucina and ammonia. The hydrate of glucina resembles the hydrate of alumina, but, when dried in the air, absorbs a considerable quantity of carbonic acid. Hydrate of glucina dissolves in potash, but is precipitated by boiling when the solution is diluted with water to a certain extent. It is likewise soluble in carbonate of potash or soda, sulphurous acid, and bisulphate of ammonia. When precipitated by ammonia, it is completely redissolved by prolonged ebullition, especially when precipitated from the oxalate or acetate.

Sulphate of Glucina.—This salt has, according to Awdejew, the formula $\text{GlO}, \text{SO}_3 + 4\text{HO}$. Debray has verified this formula by calcining one portion of the salt in powder, to determine the glucina; evaporating another portion in aqueous solution, together with a known quantity of pure lime, and calcining the residue. If the lime is in sufficient excess, nothing but water is driven off. The increase of weight of the lime, *minus* the quantity of glucina, gives the quantity of sulphuric acid, and the water is determined by difference. This method may be applied to the analysis of a great number of sulphates; lime is more convenient for the calcination than the oxide of lead generally used, because the latter is apt to oxidise and deoxidise during the calcination, thereby rendering the weight uncertain; moreover, the heating with lime may be safely performed in vessels of platinum.

A solution of sulphate of glucina dissolves zinc, with evolution of

hydrogen, which burns with a peculiar bluish flame. If the solution is dilute, a compound of sulphate of zinc with bibasic sulphate of glucina is formed; but in concentrated solutions a more basic sulphate of glucina, decomposable by water, may be formed by prolonged ebullition. A solution of sulphate of alumina, under the same circumstances, gives off hydrogen, and is converted into sulphate of zinc and insoluble subsulphate of alumina, very dense, and easy to wash. These reactions afford a method of separating glucina from alumina. The mixture of the two earths is dissolved in dilute sulphuric acid, and ammonia added till the precipitate just begins to become permanent, after which the liquid is boiled with zinc, and the water renewed as it evaporates. The alumina is then precipitated as subsulphate, while the zinc remains in solution. Nearly all the alumina is precipitated after a few hours' boiling; but to remove the last traces, the solution must be left in contact with the zinc for twenty-four hours. The zinc may be precipitated from the filtered solution by sulphuretted hydrogen, with addition of acetate of soda, and the remaining sulphate of glucina purified by crystallisation. This method is very useful for preparing a pure salt of glucina, but it will not do for quantitative analysis, because with chemically pure zinc, which it would be necessary to use for that purpose, the precipitation of the alumina is extremely slow, not being complete for several days.

The *sulphate of glucina and potash* has, according to Awdejew's analysis, the composition $\text{KO} \cdot \text{SO}_3 + \text{GlO} \cdot \text{SO}_3 + 2\text{Aq.}$ According to Berzelius's formula of glucina, this formula would become $3\text{KO} \cdot \text{SO}_3 + \text{Gl}_2\text{O}_3 \cdot 3\text{SO}_3 + 6\text{Aq.}$, which does not agree with that of the alums. Debray has obtained this salt in the form of a crystalline powder, by adding sulphuric acid to a concentrated mixture of the two sulphates.

Carbonate of Glucina.—Debray gives for this salt (without having analysed it) the formula $3\text{GlO} \cdot \text{CO}_2 + 5\text{Aq.}$; but according to the analysis of Schaffgotsch,* the formula is $5\text{GlO} \cdot \text{CO}_2 + 5\text{Aq.}$ According to Weeren,† however, this salt differs in composition according as it is separated from solution in carbonate of ammonia by boiling, or precipitated from a salt of glucina by carbonate of ammonia. The carbonate obtained by the latter method appears to be a mixture of that obtained by the former with hydrate of glucina; but even the former appears to be of variable composition. Weeren is of opinion that it is decomposed by boiling water, with separation of carbonic acid and fixation of water. It does not give off carbonic acid when heated to 100° — 110° C. in a current of dry air.

* Pogg. Ann. lvi. 101; also Gmelin's Handbook, Tr., iii. 296.

† Ibid. xcii. 91.

Carbonate of Glucina and Ammonia is obtained by boiling a solution of glucina in carbonate of ammonia, and stopping the ebullition at the moment when it begins to show turbidity. The filtered liquid, mixed with alcohol till turbidity appears, deposits the double carbonate, after a while, in transparent colourless crystals, which are very soluble in cold water, but are easily decomposed by hot water, with evolution of carbonate of ammonia. The salt is much less soluble in dilute alcohol, and nearly insoluble in absolute alcohol. It is quickly decomposed by heat, leaving glucina in the form of a crystalline powder. It does not exhale any sensible odour of ammonia at ordinary temperatures, but nevertheless decomposes after a while, and loses its lustre.

The composition of the salt is as follows:—

				Calculation.		Analysis.	
4 GlO	50.4	18.8	19.3	19.0
6 CO ₂	132.0	49.0	47.7	48.7
3 NH ₄ O	78.0	28.7	28.2	28.8
HO	9.0	3.5	3.3	1.8
<hr/> 3 (NH ₄ O . CO ₂) + 4 GlO . 3 CO ₂ + Aq				269.4	100.0	100.0	100.0

Carbonate of Glucina and Potash.—When glucina in excess is digested for some time in a solution of carbonate of potash, a liquid is obtained, which, when mixed with alcohol till it begins to show turbidity, deposits, after a while, small crystals of the double salt. This salt dissolves very readily in cold water, but is decomposed at a boiling heat, the liquid depositing ordinary carbonate of glucina. It quickly absorbs moisture from the air, and is therefore very difficult to dry. It is decomposed by heat into carbonate of potash, glucina, carbonic acid, and water. It is difficult to prepare this salt in the state of purity; moreover, it is obtained only in small quantities, and not distinctly crystallised. Hence the analysis could not be made in a very satisfactory manner; but the results agreed pretty well with the formula $3(\text{KO}, \text{CO}_2) + 4\text{GlO}, 3\text{Cl}_2 + \text{Aq}$, which is similar to that of the ammoniacal carbonate.

Oxalate of Glucina.—Oxalic acid dissolves glucina with facility, but without forming crystallised compounds; but the oxalate of glucina unites with the oxalates of potash and ammonia, forming crystalline compounds of definite form and very simple constitution.

Oxalate of Glucina and Potash.—Obtained by dissolving carbonate of glucina in binoxalate of potash. The reaction takes place in the cold, and is complete as soon as the evolution of carbonic acid ceases. At higher temperatures a large quantity of glucina dissolves, but the resulting salt is basic and uncrystallisable. The salt is white, and sparingly soluble in cold water. When heated, it first decrepi-

tates with violence, and then decomposes on exposure to the air, yielding glucina and carbonate of potash : no water is formed by the decomposition.

				Calculation.		Analysis.
KO	47.2	35.7	35.7
G1O	12.6	9.5	9.8
2 C ₂ O ₃	72.0	54.6	54.5
KO . C ₂ O ₃ + G1O . C ₂ O ₃ or C ₄ KG1O ₈				131.6	100.0	100.0

Oxalate of Glucina and Ammonia.—Prepared by treating carbonate of glucina with binoxalate of ammonia. Forms colourless crystals belonging to the right rhomboidal prismatic system. It is sometimes obtained in tabular crystals, the faces of which are rounded, and do not admit of precise measurement. It is sparingly soluble in cold, much more in hot water. Deceperitates with violence when heated, and then decomposes. The quantity of glucina in the salt was determined by boiling with nitric acid till all the oxalic acid was destroyed, evaporating the resulting nitrates to dryness, and calcining. The glucina thus obtained amounted to 11.4 per cent. (mean of three experiments). The salt burnt with oxide of copper gave 33 per cent. HO, and 79.45 CO₂. These results agree with the formula NH₄O . CO₂ + G1O . CO₂ or C₄(NH₄)G1O₈, which requires

11.4 per cent. G1O, 32.5 HO, and 79.5 CO₂.

The result of this analysis may also be used to determine the atomic weight of glucina (admitting the formula); for as the atomic weight of carbonic acid is known to be 22, and the 2 at. C₂O₃ would give 4 at. CO₂, the atomic weight of glucina will be determined by the proportion—

$$79.45 : 88 = 11.4 : x,$$

which gives $x=12.61$,—a result approaching very near to that found by Awdejew, viz. 12.64.

General Conclusions.—From these researches it follows—

1. That the metal glucinum should be placed side by side with aluminium. These bodies, intermediate between the precious and the ordinary metals, such as iron, are distinguished by the following properties:—They are permanent in the air at high as well as at ordinary temperatures; do not decompose water, even at a white heat; are not attacked by sulphur, sulphuretted hydrogen, or the alkaline sulphides; are not attacked by strong nitric acid at ordinary temperatures, and but slowly even with the aid of heat; but dissolve readily in dilute sulphuric and hydrochloric acid.

2. Glucina cannot be classed with alumina. It has been already observed (page 242), that the reasons which induced Berzelius to regard glucina as a sesquioxide were derived from the resemblance of

glucina and alumina in the hydrated state, from the volatility of the chlorides, and from the interchangeability of the oxides in minerals. This last point has been completely settled by Awdejew, whose analyses, as well as those of Damour, show that cymophane from various localities has always the same composition. The analyses of the emerald likewise show that no such substitution takes place in that mineral. With regard to the hydrates, it is true that alumina and glucina are precipitated under the same circumstances, and with the same aspect; but there the resemblance ends. Glucina, when dried in the air, absorbs carbonic acid, with which it forms a carbonate. The existence of a definitely crystallised double carbonate of ammonia and glucina constitutes another important difference between that earth and alumina. The identity of form between glucina and alumina in the crystallised state is merely an isolated fact, which would be important if the two oxides possessed similar chemical properties, but not otherwise. Now these oxides differ both in their behaviour when heated, and in their reactions with more basic oxides. Glucina volatilises like magnesia without melting, whereas alumina fuses under the same circumstances. Glucina cannot be fused with lime like alumina: to enable the fusion to take place, the presence of another body is required to play the part of an acid,—such as silica or alumina. In this respect, again, glucina resembles magnesia.

Chloride of glucinum exhibits at first sight considerable resemblance to chloride of aluminium, but a closer examination shows that the resemblance does not go far. Chloride of glucinum is less volatile than chloride of aluminium: thus, when a mixture of finely-pounded emerald and charcoal, made into a paste with oil, is calcined in a crucible, then powdered and heated in a porcelain tube through which chlorine gas is passed, chloride of glucinum and chloride of aluminium are formed together; but the chloride of glucinum passes over first, and may be separately condensed. Chloride of glucinum, in fact, approaches in volatility more nearly to protochloride of iron than to chloride of aluminium: it is about as volatile as chloride of zinc. Chloride of aluminium unites with the alkaline chlorides, forming compounds which may be called spinelles, and are represented by the general formula— $MCl + Al_2Cl_3$ (Deville); but chloride of glucinum does not form any similar compounds.

Another argument in favour of the formula G_2O is derived from the greater simplicity of the formulæ which it gives for the salts of glucina: thus, if glucina were regarded as G_2O_3 , the formula of carbonate of glucina and potash would be $3(KO \cdot CO_2) + G_2O_3 \cdot 3CO_2$; and that of the oxalate of glucina and ammonia—



It must, however, be remembered that glucina does not exhibit any

very close analogy to the class of protoxides. It is not isomorphous with lime or magnesia. Cymophane may be represented by the general formula of the spinelles— $\text{GlO}, \text{Al}_2\text{O}_3$; but the dissimilarity of its crystalline form prevents it from being included in that class of minerals. The emerald, also, differs completely in crystalline form from the generality of silicates of the same composition, whose general formula is— $\text{MO} \cdot \text{SiO}_3 + \text{M}'_2\text{O}_3, 3\text{SiO}_3$. Neither is there any greater analogy between the double sulphates, carbonates, and oxalates of glucina, and those of lime or magnesia. On the whole, glucina appears to be intermediate in its properties between the protoxides and sesquioxides.

On some Salts of Cadmium.*

By Carl von Hauer.

1. *Sulphate of Cadmium*, $\text{CdO} \cdot \text{SO}_3 + \text{HO}$.—When cadmium or oxide of cadmium is dissolved in an excess of dilute sulphuric acid, and the solution is concentrated by boiling, a salt is obtained which separates in verrucose crystals. The salt crystallises immediately on the cooling of the solution, and corresponds in its constitution with the sulphate of cadmium with 1 atom of water obtained by Kühn.

As the solution of the metallic cadmium in sulphuric acid only takes place slowly, even with the aid of heat, it is advisable to add a little nitric acid occasionally, in order to facilitate the oxidation. This salt is also obtained when concentrated sulphuric acid is added to a boiling saturated solution of sulphate of cadmium; it is immediately thrown down in the form of a fine crystalline powder, and may be almost entirely freed from the adhering sulphuric acid by pressure between blotting-paper. The salt, prepared in three different manners, gave the following results on analysis:—

Calculated.				Found.		
CdO . . .	64	56·63		56·63	56·70	56·56
SO ₃ . . .	40	35·39		35·39	35·45	35·54
HO . . .	9	7·98		7·98	7·85	7·90
	<hr/>	<hr/>		<hr/>	<hr/>	<hr/>
	110	100·00		100·00	100·00	100·00

The salt does not effloresce in the air. At 100° C. the loss was 7·85 and 7·90 per cent. in two experiments, so that the salt loses the whole of its water of crystallisation at this temperature, and leaves dry sul-

* Wien. Akad. Ber. xv. 23.

phate of cadmium. At a red heat it gives off sulphuric acid, and leaves sesquisulphate of cadmium.

2. *Sulphate of Cadmium*, $3(\text{CdO} \cdot \text{SO}_3) + 8\text{HO}$, was obtained by the spontaneous evaporation of a saturated solution. The crystals were determined by Rammelsberg, who found that their form was exactly that of Stromeyer's salt, $\text{CdO}, \text{SO}_3 + 4\text{HO}$. This salt is perfectly stable in the air. At 100°C . it loses 11.78 to 11.84 per cent., or nearly 3 atoms of water; it is then perfectly opaque. At a slight red heat the remainder of the water is driven off, without any loss of sulphuric acid; at a stronger red heat, half the sulphuric acid is expelled, and there remains sesquisulphate of cadmium. By long-continued calcination a portion of the remaining sulphuric acid is driven off; the mass is partially fused, and appears brown from the production of free oxide.

The saturated watery solution of sulphate of cadmium boils at 102°C . At 23° , 1 part of water dissolves 0.59 part of anhydrous sulphate of cadmium. Its solubility in hot water is not much greater. The author's analysis led to the above formula:—

		Calculated.		Found.		
3CdO	. . 192	50.00	49.75	49.68	49.20	
3SO ₃	. . 120	31.25	31.35	31.27	31.94	
8HO	. . 72	18.75	18.90	19.05	18.86	
	<hr/> 384	<hr/> 100.00	<hr/> 100.00	<hr/> 100.00	<hr/> 100.00	<hr/> 100.00

Sulphate of cadmium dissolves in large quantity in concentrated ammonia, with evolution of heat. When the solution is diluted with water, a partial precipitation of hydrated oxide of cadmium takes place. The solution of sulphate of cadmium in ammonia is not immediately precipitated by carbonate of ammonia, but precipitation takes place on the application of heat. If the solution in caustic ammonia be evaporated, it becomes covered with a film, and an uncrystallisable mass is deposited, which dissolves but sparingly in water. This takes place during the spontaneous evaporation of the fluid, but then requires a long time. A cold saturated solution of sulphate of cadmium is not precipitated by alcohol. A thick oily fluid settles to the bottom of the vessel, and the supernatant fluid is at first a little turbid, but soon becomes clear; after a time some rather large crystals are formed at the bottom of the vessel, which appeared, both from measurement and analysis, to be the salt $3(\text{CdO}, \text{SO}_3) + 8\text{HO}$.

3. *Nitrate of Cadmium*, $\text{CdO}, \text{NO}_3 + 4\text{HO}$, is obtained by dissolving carbonate of cadmium in dilute nitric acid, evaporating the solution, and leaving it to cool. As the salt is very soluble, crystallisation only takes place when the fluid is much concentrated. It crystallises, as stated by Stromeyer, in acicular and columnar crystals united in a radiate form. It deliquesces in the air, as stated by

Meissner. At 212° F. it melts in its water of crystallisation. The analysis of the air-dried salt gave—

		Calculated.	Stromeyer.	Hauer.
CdO . . .	64	41·56	42·15	40·78
NO ₅ . . .	54	35·07	35·78	34·41
4HO . . .	36	23·37	22·07	24·81
	<hr/>	<hr/>	<hr/>	<hr/>
	154	100·00	100·00	100·00

4. *Ammonio-chloride of Cadmium*.—According to Croft, dry chloride of cadmium absorbs 3 atoms of ammonia. The compound thus formed, which has the formula $3\text{H}_3\text{N} \cdot \text{CdCl}$, gives off ammonia in the air until it becomes inodorous. The loss of ammonia amounts to 2 atoms, so that there remains a compound of the formula $\text{H}_3\text{N} + \text{CdCl}$. A compound similar to this, and also containing only 1 atom of ammonia, may be obtained, according to Croft, by dissolving chloride of cadmium in heated liquid ammonia, and leaving the solution to cool, when the compound is deposited in crystalline grains. The loss of weight on heating was 16·63 per cent. H_3N .

By the addition of hydrochloric acid to a solution of chloride of cadmium in ammonia, Schüler obtained a fine crystalline powder, the constitution of which he found to be $3\text{H}_3\text{N} \cdot \text{CdCl}$: he states that this is the same salt that is obtained by the spontaneous evaporation of a solution of chloride of cadmium in ammonia. By this process the author has obtained a salt with only 1 atom of ammonia, which is consequently the same as that described by Croft,—a proof that this compound loses 2 atoms of ammonia just as quickly as that which is produced by passing ammoniacal gas over chloride of calcium. This loss of ammonia must take place during drying. For analysis, the salt was dried between blotting-paper. It gave—

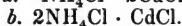
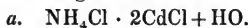
		Calculated.	Found.
H ₃ N . . .	17	15·68	16·15
Cd . . .	56	51·66	51·64
Cl . . .	35·4	32·65	32·21
	<hr/>	<hr/>	<hr/>
	108·4	100·00	100·00

If hot liquid ammonia be used in the preparation of this compound, a little precipitated hydrated oxide mixes with it during cooling; it is therefore better to mix ammonia with a cold aqueous solution of chloride of cadmium, until the precipitate which is formed at first is again dissolved, leaving the solution to evaporate spontaneously, when crystalline crusts are deposited. It is nearly insoluble in water.

When carbonate of cadmium, or the anhydrous or hydrated oxide, is treated with an aqueous solution of sal-ammonia, it dissolves in considerable quantity with evolution of ammonia. The filtered solution

yields crystalline crusts on evaporation; but these differ very considerably in the proportion of chloride of cadmium and chloride of ammonium, according to the length of the reaction. But if one of the above compounds be boiled for a long time with sal-ammoniac, then filtered and left to cool, anhydrous crystallised chloride of cadmium and ammonium is deposited, having the composition $2\text{H}_4\text{NCl} + \text{CdCl}$.

5. *Chloride of Cadmium and Ammonium*.—Croft has prepared two salts of chloride of cadmium and ammonium, which, according to the author, have the following formulæ:—



6. *Chloride of Cadmium and Potassium* forms two salts of exactly similar composition to the two preceding:—

a. $\text{KCl} + 2\text{CdCl} + \text{HO}$.—This salt is produced when equivalents of the two constituents are dissolved together and left to spontaneous evaporation; it forms silky needles united in tufts. The salt is very soluble; when dried over sulphuric acid, it partially loses its water of crystallisation, and this water is entirely driven off at 100°C .; in either case the salt becomes opaque. It undergoes no change at the ordinary temperature of a room. When strongly heated, it melts readily, but loses a part of its chlorine, and is then no longer soluble in water. When dissolved in water, it crystallises again unchanged from the solution. Its analysis gave—

		Calculated.	Found.
K . . .	39.2	14.71	13.93
2Cd . . .	112	42.04	42.55
3Cl . . .	106.2	39.86	49.24
HO . . .	9	3.37	4.58
	<hr/> 266.4	<hr/> 100.00	<hr/> 100.00

b. $2\text{KCl} \cdot \text{CdCl}$.—When the salt a has been removed from its mother-liquor, the latter furnishes, on further spontaneous evaporation, large limpid crystals, similar to those of nitrate of soda, and constituted according to the formula $2\text{KCl} \cdot \text{CdCl}$. This salt is remarkable for its great facility of crystallisation: whilst the corresponding ammoniacal double salt is generally obtained in scalariform groups of dull crystals, the potash-salt shoots out readily on all sides into perfectly formed transparent crystals, with brilliantly shining faces. This salt can be obtained directly only by mixing aqueous solutions of at least 3 atoms of chloride of potassium with 1 atom of chloride of cadmium, and leaving the mixture to crystallise.

This salt is rather less soluble in water than the preceding. If the aqueous solution be left to spontaneous evaporation, the salt a first of all crystallises again from it. It melts when strongly heated,

and then behaves like the preceding potassium-salt. It undergoes no change in the air. The two salts $2\text{H}_4\text{NCl} + \text{CdCl}$ and $2\text{KCl} + \text{CdCl}$ are isomorphous. The analysis of the potassium-salt gave—

		Calculated.	Found.
2K . . .	78·4	32·58	32·72
Cd . . .	56	23·28	23·66
3Cl . . .	106·2	44·14	43·62
	<hr/> 240·6	<hr/> 100·00	<hr/> 100·00

7. *Chloride of Cadmium and Sodium*, $\text{NaCl} \cdot \text{CdCl} + 3\text{HO}$ (air-dried).—A solution containing equivalents of chloride of cadmium and chloride of sodium, concentrated by heat, soon deposits this double salt; it consists of small, dull, verrucose crystals, which are constituted according to the above formula, as stated by Croft. When dried at 100°C ., it loses 12·30 per cent. = 2 atoms water; the third atom is only expelled between 150° and 160°C . From this it would appear that the salt has 2 atoms of water of crystallisation and 1 atom of constitution-water, the latter being more obstinately retained. The salt may consequently be regarded as a hydrated compound of chloride of sodium with hydrochlorate of cadmicoxid, the formula of which would be $(\text{NaCl} + \text{CdO} \cdot \text{HCl}) + 2\text{HO}$; and the salt dried at 212°F ., after losing its water of crystallisation, would have the formula $\text{NaCl} + \text{CdO} \cdot \text{HCl}$. When heated, it melts, and behaves like the potassium-salts. It undergoes no change in the air.

8. *Chloride of Cadmium and Barium*, $\text{BaCl} \cdot \text{CdCl} + 4\text{HO}$.—If aqueous solutions of chloride of barium and chloride of cadmium be mixed, and left to evaporate spontaneously, a salt is produced when the chloride of barium is in excess, which forms small crystals, is difficult of solution in water, and appears to contain an indeterminate proportion of chloride of cadmium. When this has been removed, the mother-liquor furnishes large well-formed crystals, which are sometimes transparent when small, but lose their transparency as they grow larger, although their faces exhibit a brilliant lustre. By placing these crystals in recently saturated liquor, they may be obtained in the course of a few weeks more than an inch in length. When solutions of equivalents of the two salts are mixed, the salt is obtained directly. It is produced in the same way by spontaneous evaporation and by heat. Analysis:—

		Calculated.	Found.
Ba . . .	68·6	29·64	29·62
Cd . . .	56	24·20	24·17
Cl . . .	70·8	30·59	30·56
HO . . .	36	15·56	15·65
	<hr/> 231·4	<hr/> 100·00	<hr/> 100·00

The salt is perfectly stable in the air, dissolves readily in water, and crystallises unchanged from the solution. The above analysis is of the air-dried salt. At 100°C . it loses 8.82 per cent. or 2 atoms of water; the other 2 atoms are only expelled at 160°C .; it has then a porcelain-like appearance. Judging from this behaviour of the water, the constitution of the salt might be more exactly expressed by the formula $(\text{BaO} \cdot \text{HCl} + \text{HO}) + (\text{CdO} \cdot \text{HCl} + \text{HO})$, as it indicates more distinctly the part which the water plays in it; it is a simple compound of hydrated hydrochlorate of baryta and hydrated hydrochlorate of cadmic oxide. The composition of the salt dried at 100°C ., at which temperature it loses its water of crystallisation, is consequently $(\text{BaO} \cdot \text{HCl}) + (\text{CdO} \cdot \text{HCl})$; and when dried at 160°F ., when its constitutional water is expelled, $\text{BaCl} + \text{CdCl}$. When heated to redness, it fuses after loss of water, forming a clear colourless fluid, which on cooling is not crystalline, and has an enamel-like appearance. The fused mass is no longer perfectly soluble in water; it has therefore probably lost a part of its chlorine.

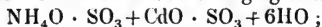
9. *Bromide of Cadmium and Bromide of Potassium* form the same salts as chloride of ammonium and chloride of cadmium, namely—

a. $\text{KBr} \cdot 2\text{CdBr} + \text{HO}$; and

b. $2(\text{KBr}) \cdot \text{CdBr}$, which is deposited from the mother-liquor of the preceding. They are isomorphous with the above-described chlorides.

The bromide of cadmium employed in the preparation of these two salts was obtained by bringing metallic cadmium in contact with bromine and water. In the distillation of oxide of cadmium with charcoal for the preparation of the metal, the latter is obtained not only in large globules, but also in a finely divided state, of a greyish colour, very similar to platinum-black. In this form the metal is best fitted for combining with bromine: the combination is effected in a short time, and with a considerable evolution of heat. As by this means, even when a large quantity of water is present, a considerable quantity of the bromine is expelled in the form of vapour, it is advisable to bring the two substances in contact in a closed flask, and to put this into cold water if the heat be too great. The solution, which is at first red, soon becomes perfectly colourless, as the combination goes on very rapidly.

10. *Sulphate of Cadmium and Ammonium*.—This salt, which was first prepared by Mitscherlich, is readily obtained in large well-formed crystals, by the spontaneous evaporation of a solution containing the two salts in equivalent proportions. The crystals undergo no change in the air, and possess a peculiar fatty lustre, and are fatty to the touch; they are only transparent when small, larger crystals being always opaque. The composition of the salt agrees with the general formula of the numerous salts belonging to this series,—



but to obtain this quantity of water, the drying must be very carefully conducted. If large crystals are analysed, without drying them in a pounded state, a quantity of water is obtained much greater than that which is required by the above formula, even though the crystals may have been long in drying; for they always contain water mechanically, and retain it very obstinately. Analysis:—

	Calculated.	Found.
NH ₃ . . . 17	7.59	7.66
CdO . . . 64	28.57	28.50
2SO ₃ . . . 80	35.71	35.85
7HO . . . 63	28.12	27.99
224	100.00	100.00

The salt cannot be dried over sulphuric acid, as it effloresces. When dried at 212°, it loses 26.60 per cent. or 6 atoms of water; the last atom, which is united with the ammonia, is only driven off by a higher temperature, simultaneously with sulphate of ammonia. If the salt be directly exposed to a high temperature, it swells up, and melts partially in the water of crystallisation, and the sulphate of ammonia is completely driven off together with the water; sulphuric acid is afterwards expelled, and the residue consists of sesquisulphate of cadmium. The salt may be recrystallised without alteration by dissolving it in a small quantity of water.

11. *Sulphate of Cadmium and Potassium*, KO · SO₃ + CdO · SO₃ + 6HO.—This salt is obtained with difficulty, as the sulphate of potash, which is less soluble, has a greater tendency to crystallise. It is best prepared by saturating a solution of bisulphate of potash with carbonate of cadmium, adding a little sulphuric acid, and leaving the solution to spontaneous evaporation. It could not be obtained pure by concentrating the solution by heat and leaving it to cool. Even the formed crystals are decomposed when the temperature of the mother-liquor changes a little. It is scarcely possible to obtain large crystals in a state of purity, as they are generally covered with small crystals of sulphate of potash. In its crystalline form and constitution the salt resembles the preceding. When the crystals are taken out of the mother-liquor, they exhibit beautifully shining faces, but soon become dull; the efflorescence goes on so rapidly that it is difficult to get the salt for analysis with its whole 6 atoms of water, unless it is employed with the mother-liquor adhering to it. Analysis:—

	Calculated.	Found.
KO . . . 47.2	19.25	20.23
CdO . . . 64	26.10	26.54
2SO ₃ . . . 80	32.62	33.73
6HO . . . 54	19.50	19.50
245.2	100.00	100.00

If the salt has been kept for a few hours in a heated room, only 4 or 5 atoms, or even less water, will be found.

12. *Sulphate of Cadmium and Sodium* is obtained by mixing the two salts in equivalent proportions. The crystallisation takes place with difficulty, and only when the solution is much concentrated. The salt forms small verrucose crystals, like those of sulphate of cadmium with 1 atom of water. In the air-dried state it contains 2 atoms of water, and is consequently composed according to the formula $\text{NaO} \cdot \text{SO}_3 + \text{CdO} \cdot \text{SO}_3 + 2\text{HO}$. Analysis:—

	Calculated.	Found.
NaO . . . 31	16·06	16·37
CdO . . . 64	33·16	32·71
2SO ₃ . . . 80	41·45	41·57
2HO . . . 18	9·32	9·35
103	100·00	100·00

This salt appears to be obtained with less difficulty when a slight excess of acid is present.

On the Preparation of the Sulphochloride of Mercury in the Dry Way.*

By R. Schneider.

H. ROSE has long since shown that the white precipitate formed during the first period of decomposition by passing sulphuretted hydrogen gas into a solution of mercuric chloride, is a compound of chloride and sulphide of mercury in such proportions as to be expressed by the formula $\text{HgCl} \cdot 2\text{HgS}$. According to H. Rose, the same compound may be obtained by boiling moist black sulphide of mercury with an excess of a solution of mercuric chloride. When prepared by either of these methods, it has the appearance of a white amorphous powder, which is insoluble in boiling water and simple acids, but is readily decomposed by nitrohydrochloric acid or potash, in the latter case leaving a residue of black oxysulphide of mercury.

This compound may also be obtained with ease and certainty in the dry way, by enclosing sulphide of mercury (either black or red) with an excess of mercuric chloride in closed glass tubes, when, on the application of heat, the sulphide of mercury dissolves in the fusing chloride, forming a yellowish-brown fluid, which, on cooling, solidifies into a pearl-grey, enamel-like mass, a mixture of mercuric chloride

* Pogg. Ann. xcv. 167.

and sulphochloride. The operation is best performed by means of a Berzelius lamp, at about 662° to 752° F.; and if the tubes are formed of strong hard glass, and well closed at the ends, it generally goes on without any disturbance. The mercuric chloride must be employed in considerable excess if the sulphide is to be completely dissolved; the quantity should be about 8 to 10 parts of the chloride to 1 of sulphide (cinnabar); if less of the former be used, the cinnabar is certainly converted into sulphochloride, but a portion of the latter remains undissolved as a white powder. The excess of mercuric chloride may be completely extracted from the solid mass by treatment with boiling water; the sulphochloride then remains in the form of a dingy white, distinctly crystalline powder. Its analysis gave—

	Found.	Calculated.
Hg	81.26	81.52
S	—	8.57
Cl	9.68	9.91

In its properties and chemical behaviour, the compound prepared in the dry way nearly agrees with that obtained in the humid way. It is, however, essentially distinguished from it by its crystalline form, and also by the circumstance that when agitated in water it rapidly sinks to the bottom, and may be very easily washed upon the filter, whilst that which is prepared in the humid way remains long suspended in the fluid, and causes difficulties in filtration from producing turbidity in the filtrate.

On an easy Method of Purifying Sulphuric Acid from Arsenic.*

By A. Buchner.

ARSENIOUS ACID, as is well known, is easily changed by the action of hydrochloric acid into the much more volatile chloride of arsenic. If arsenious acid be dissolved in hydrochloric acid, or if a liquid containing arsenious acid be mixed with hydrochloric acid, and then a sufficient quantity of concentrated sulphuric acid be added, chloride of arsenic, as Liebig has shown, will separate out in oily drops, and as such may be distilled off. Chloride of arsenic boils at 132° C., and volatilises with hydrochloric acid vapour much under its boiling point, while concentrated sulphuric acid boils at 325° to 327° C.

I am not aware whether these facts have been made available for purifying sulphuric acid from arsenious acid,† but experiments have shown

* Ann. Ch. Pharm. xciv. 241.

† J. Löwe recommended, for the purification of sulphuric acid from arsenious acid, the addition of finely-powdered chloride of sodium to the hot acid (Chem. Gaz. xii. 464).

me that they form the basis for such a method of purification. In fact, if sulphuric acid containing arsenic be mixed with a little hydrochloric acid, and warmed,—or better, if a moderate stream of hydrochloric acid gas be passed through the heated sulphuric acid,—all the arsenic is rapidly removed as chloride of arsenic. I have purposely dissolved a large quantity of arsenious acid in sulphuric acid, and then treated it in this manner. Soon the arsenic was so perfectly removed, that Marsh's apparatus gave no trace of arsenic even after some time. After passing the hydrochloric acid through the liquid, the heat may be continued for a little time, in order to drive off every trace of hydrochloric acid, if necessary.

I consider this process the only possible one for preparing sulphuric acid pure for chemico-legal investigations. It is known that sulphuric acid cannot be freed from arsenious acid by rectification, because their boiling points are too near, and because the sulphuric acid is the more volatile of the two; and the precipitation of the arsenious acid out of sulphuric acid by sulphuretted hydrogen is too unpleasant, and takes too much time.

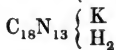
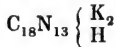
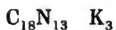
This process offers also the advantage, that any nitrous acid which may be present is removed in the form of chloride of nitric oxide.

On the Mellonides.*

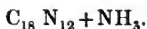
By J. Liebig.

AN examination of the mellonides has led me to an incontestable proof that the radical of those compounds contains no trace of hydrogen.

The composition of hydromellonic acid is expressed by the formula $C_{18}N_{13}H_3$. This compound should be a tribasic acid, capable of forming with potassium three distinct compounds, the constitution of which may be expressed by the formulæ—



The composition of the mellonide of silver would be expressed by $C_{18}N_{13}Ag_3$. If hydromellonic acid be compared with some compounds of the same group, it may be considered as constituted in the following manner :—

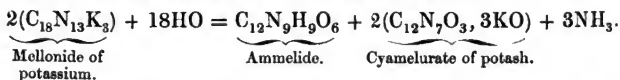


* Compt. rend. xl. 1077.

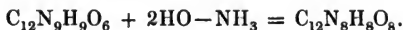
The following products might then be connected with this compound; namely—

Melam	$C_{12}N_8 + 3NH_3$
Melamine	$C_6N_4 + 2NH_3$
Ammeline	$C_6N_4 + 2NH_3 + 2HO$
Ammelide	$2(C_6N_4) + NH_3 + 6HO$
Cyamaluric acid	$C_{12}N_7O_3 + 3HO$

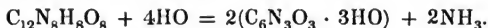
If an excess of potash is made to act upon mellonide of potassium with the aid of heat, this compound is decomposed by the intervention of 18 molecules of water, forming ammonia, ammelide, and cyameluric acid, as shown in the following equation:—



By continuing the action of the potash, the ammelide fixes the elements of 2 molecules of water, and loses 1 molecule of ammonia, becoming converted into the compound, the formation of which, by the action of a proper degree of heat upon urea, has already been signalled by Wöhler and myself. Thus—



The latter compound is finally converted into cyanuric acid by the prolonged action of the potash. Thus—



On some Compounds of Stibethylum.*

by R. Löwig.

Iodide of Stibethylum, $SbAe_4I + 3HO$.—This body is formed when stibethyl and iodide of ethyl are allowed to act upon each other. The two fluids mix together, but only act upon each other slowly. When enclosed by fusion in a glass tube, and heated to $100^\circ C.$, the combination takes place very rapidly, and much heat is suddenly set free. The best mode of obtaining it is by mixing equal parts of stibethyl and iodide of ethyl, putting the mixture into a retort filled with carbonic acid, nearly filling this with water, and closing it by fusion. The retort is then laid in boiling water, whereupon the combination takes place in two or three hours. The solution

* J. pr. Chem. lxiv. 415.

is allowed to cool and evaporate on the water-bath, during which process it acquires a somewhat yellow colour, which, however, may be removed by the addition of a few drops of ammonia.

Properties.—Iodide of stibethylum crystallises in beautiful hexagonal prisms, often an inch in length, or in small pointed crystals, which acquire a yellowish colour in the air. It has a very bitter taste. 19·02 parts of it dissolve in 100 parts of water at 20° C.; it dissolves more easily in absolute alcohol, but in æther with more difficulty than in water. The analyses (a) are of the hydrated, and (b) of the anhydrous salts:—

		Calculated.	Found.		Calculated.	Found.	
			(a)	(a)		(b)	(b)
Sb	129	32·33	—	—	34·33	—	—
16C	96	24·06	24·25	24·03	25·80	25·75	25·84
23H	23	5·77	6·28	5·95	5·47	5·64	5·58
I	127	31·83	32·24	31·88	34·40	34·38	34·17
3O	24	6·01	—	—	—	—	—
		399	100·00		100·00		

During the crystallisation of iodide of stibethylum, especially when it separates from warm solutions, another salt is often formed, with a different amount of water, 2 (SbAc₄I) + 3HO.

Iodide of Stibethylum and Mercury, 3HgI + (SbAc₄)I.—When a solution of mercuric chloride is added to a solution of iodide of stibethylum, a white precipitate is produced, which melts into an oily fluid even at a gentle heat.

This salt is insoluble in water and ether, and dissolves with difficulty in boiling alcohol. It crystallises from this solution in columnar crystals. If the precipitate be allowed to melt under water of 70° C., it solidifies to a white mass, and only exhibits single red spots, but becomes entirely red after some time. If the mass which has become red be dissolved in boiling alcóhol, the white salt separates again in hexagonal prisms. Both forms of the salt have the same composition, but the red crystals appear to belong to the regular system. This salt gave on analysis—

		Calculated.	Found.	
			—	—
SbAc ₄	245	23·27	—	—
3Hg	300	28·49	29·30	28·40
4I	508	48·24	49·00	48·60
		1053	100·00	

A similar compound, 3HgI + 2(SbAc₄I), is obtained by adding iodide of mercury to a hot solution of iodide of stibethylum, until it

no longer loses its red colour. The conversion of the excess of iodide of mercury is then effected by a fresh addition of iodide of stibethylum. None of the latter remains in the fluid; the precipitate melts when heated, forming a yellow oil. Analysis:—

				Calculated.		Found.	
2SbAc ₄	.	.	490	34.38		—	—
3Hg	.	.	300	21.06		20.86	21.80
5I	.	.	635	44.32		44.56	44.52
				—	—		
				1425	100.00		

Chloride of Stibethylum, (SbAc₄)Cl + 3HO, is obtained by saturating oxide of stibethylum with hydrochloric acid, or by decomposing 4 atoms of iodide of stibethylum with 3 atoms of mercuric chloride, by which means 3 atoms of chloride of stibethylum are obtained. In the latter case, the solution contains neither iodine nor mercury. The salt crystallises, and deliquesces more readily even than chloride of calcium. It loses its water of crystallisation on the water-bath. It has a strongly bitter taste. The analysis of the dry salt gave—

				Calculated.		Found.	
Sb	.	.	129	56.03		—	—
16C	.	.	96	34.29		33.29	33.21
20H	.	.	20	7.01		7.76	7.63
Cl	.	.	35.5	12.67		11.13	12.50
				—	—		
				280.5	100.00		

Chloride of Stibethylum and Mercury.—Compounds exactly similar to those of iodide of mercury with iodide of stibethylum are obtained by bringing in contact chloride of mercury and iodide or chloride of stibethylum. 1 atom of iodide of stibethylum with 3 atoms of chloride of mercury furnish the iodine compound which melts under water, whilst the water takes up the corresponding chloride, 3HgCl + (SbAc₄)Cl. If concentrated solutions of chloride of stibethylum and mercuric chloride be mixed, a compound of the formula 3HgCl + 2(SbAc₄)Cl is obtained. The former salt is soluble in alcohol and water; the latter forms a white powder, which is difficult of solution in water.

Chloride of Stibethylum and Platinum, 3PtCl₂ + 2SbAc₄Cl.—This salt is produced by mixing a somewhat dilute alcoholic solution of chloride of stibethylum with a similar solution of chloride of platinum, and evaporating the mixture. It is a fine yellow compound, tolerably soluble in water and alcohol, which yields 68.6,

67·2, and 69·2 per cent. of platinochloride of platinum. (Calculation, 68·53 per cent.)

Bromide of Stibethylum, $(\text{StAe}_4)\text{Br}$, was obtained by saturating oxide of stibethylammonium with hydrobromic acid. It crystallises in dazzling white acicular crystals, which dissolve very readily in water and alcohol, and do not deliquesce in the air. Analyses gave 24·39 and 24·37 of bromine. With oxide of stibethylum bromine appears to form bromide and bromate of stibethylum.

Hydrated Oxide of Stibethylum, $\text{StAe}_4\text{O}\cdot\text{HO}$, is obtained by decomposing iodide of stibethylum with oxide of silver. Traces of dissolved oxide of silver are removed by the careful addition of hydrochloric acid. The fluid is evaporated *in vacuo*, when the hydrate is obtained in the form of a thick, colourless, oily fluid, of a strongly alkaline and intensely bitter taste, which quickly renders litmus-paper blue. It dissolves in water and alcohol in all proportions, but is insoluble in ether. It sets ammonia free from its compounds, and precipitates the oxides of the heavy metals. Oxide of tin and alumina are again dissolved by the excess of the alkali. The salts of the alkaline earths are not decomposed by the base.

The salts are produced by bringing the base in contact with the acids, or by double decomposition. They have a strong bitter taste.

The sulphate, $(\text{SbAe}_4)\text{O} \cdot \text{SO}_3$, crystallises.

The nitrate, $(\text{SbAe}_4)\text{O} \cdot \text{NO}_5$, crystallises.

The carbonate, $(\text{SbAe}_4)\text{O} \cdot \text{CO}_2$, is a tough deliquescent mass.

The formiate, $(\text{SbAe}_4)\text{O} \cdot \text{FoO}_3$, forms acicular crystals, difficult of solution.

The acetate, $(\text{SbAe}_4)\text{O} \cdot \text{AcO}_3$, forms more soluble acicular crystals.

The succinate, $(\text{SbAe}_4)\text{O} \cdot \text{SuO}_6$, does not crystallise.

The oxalate, $(\text{SbAe}_4)\text{O} \cdot \text{C}_2\text{O}_3$, crystallises.

The tartrate, $(\text{SbAe}_4)\text{O} \cdot \text{C}_4\text{H}_2\text{O}_5$, forms large deliquescent crystals.

The bitartrate, $(\text{SbAe}_4)\text{O} \cdot 2(\text{C}_4\text{H}_2\text{O}_5)$, forms fine needles.

The racemate, $(\text{SbAe}_4) \cdot \text{OC}_4\text{H}_2\text{O}_5$, forms large deliquescent crystals.

Sulphide of Stibethylum, $(\text{SbAe}_4)\text{S}$, is obtained by treating oxide of stibethylum with sulphuretted hydrogen. It is evaporated without access of air, and forms a yellowish oily fluid, which does not crystallise; it dissolves readily in water and alcohol, and behaves towards the salts of the metals like sulphide of potassium.

On Butylic Alcohol.*

By A. Wurtz.

THIS alcohol is obtained from the fusel-oil which remains after the rectification of the alcohol obtained from beet-molasses. Different samples of this fusel oil, however, contain very different quantities of the alcohol, and many none at all. To separate the butylic alcohol, Wurtz collects apart the portions which distil over between 80° and 105° , 105° and 115° , 115° and 125° C. The first portion is washed with water, the oily layer which separates repeatedly rectified, the portion which passes over above 104° being each time collected apart. The latter is united with the portion which passed over between 105° and 115° , and with so much of the last portion (which passed over between 115° and 125°) as, in repeated rectifications of the latter, passes over below 115° . All the liquid which has distilled over between 105° and 115° is then boiled for forty-eight hours with a strong solution of caustic potash, in such a manner that the volatilised portion may condense and flow back again; the impure butylic alcohol is then distilled over, separated from the water which passes over at the same time, more completely dehydrated by leaving it for twenty-four hours in contact with half its weight of caustic potash, and then distilled. The distillate is repeatedly rectified, and the portion which goes over between 108° and 110° collected apart: if the boiling point remains constant between these limits during the whole of the distillation, the butylic alcohol is very nearly pure. The process of purification may be shortened by causing the vapour to pass from the distilling flask through an upright tube having two bulbs blown on it, and fitted with a thermometer which is immersed in the vapour at the top before it reaches the condensing apparatus. The less volatile portion then condenses in the tube and runs back into the flask, and the separation of the more and less volatile portions is thereby greatly facilitated. Butylic alcohol purified as above, and boiling at 110° , gave results nearly agreeing with the formula $C_4H_{10}O_2$; viz.—

	Calculated.	Analysis.		
		I.	II.	III.
Carbon .	64.86	64.55	64.49	64.94
Hydrogen	13.51	13.90	13.53	13.65

For complete purification, Wurtz converted the butylic alcohol into iodide of butyl, which boils at 121° C., and is easily separated by fractional distillation from iodide of ethyl, which boils at 78° , and iodide of amyl, boiling at 146° , transformed the iodide of butyl into

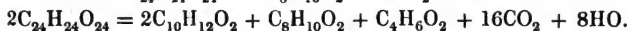
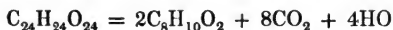
* Ann. Ch. Phys. [3], xlii. 129; Ann. Ch. Pharm. xciii. 107.

acetate by means of acetate of silver ; and decomposed the latter by continuous boiling with concentrated solution of potash, the volatilised portion being condensed and made to run back ; the butylic alcohol was then poured off and rectified over caustic baryta.

Butylic alcohol thus purified is a colourless liquid, more mobile than amylic alcohol, and having an odour similar to that of the latter, but less pungent and more vinous : it rotates the plane of polarisation of a ray of light ; exhibits the composition marked III. in the above table ; and boils at 109° C. Sp. gr. = 0.8032 at 18° .5 C. Vapour density = 2.589. The formula $C_8H_{10}O_2$ gives 2.565 for a condensation to 4 volumes.

Butylic alcohol readily takes fire on the approach of a burning body, and burns with a bright flame. It dissolves in $10\frac{1}{2}$ times its weight of water at 18° , and is precipitated from that solution by chloride of calcium, chloride of sodium, or other soluble salt, in the form of an oily layer. It dissolves chloride of calcium, and forms a crystalline compound therewith. Potassium converts it, with evolution of hydrogen, into $C_8H_9 \left\{ \begin{smallmatrix} H \\ K \end{smallmatrix} \right\} O_2$. When the alcohol is dropped upon soda-lime heated to 250° , hydrogen gas is evolved, and a salt of butyric acid formed. Sulphuric acid acts violently on butylic alcohol, the mixture becoming heated and coloured. When the alcohol is mixed with sulphuric acid, sulphurous acid is evolved, and an oily layer separates, consisting chiefly of hydrocarbons polymeric with butylene. When butylic alcohol is quickly mixed with excess of sulphuric acid, a small quantity of gas is evolved with great rise of temperature : by the application of a gentle heat, the gas may be obtained in larger quantity ; it consists chiefly of butylene, together with carbonic and sulphurous acid. When the alcohol is gradually mixed with an equal volume of sulphuric acid, and the mixture kept cool, sulphobutylic acid is produced.

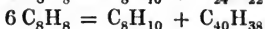
The formation of butylic alcohol from grape-sugar, alone or simultaneously with vinic and amylic alcohols, is expressed by the following equations :—



Wurtz searched in vain for propylic alcohol in the fusel-oil from beet-molasses. Some samples of this fusel-oil yielded, by distillation, a small quantity of a liquid which distilled over at 160° and upwards : this, however, was not an alcohol, but a mixture of certain compound ethers of the amyl series.

Action of Chloride of Zinc on Butylic Alcohol.—Butylic alcohol dissolves recently fused chloride of zinc at ordinary temperatures, forming with it a syrupy liquid. Heated with excess of chloride of zinc, it is decomposed, giving off, first butylene gas, C_8H_8 , afterwards

a mixture of that gas with hydride of butyl, C_8H_{10} . On passing the evolved gases through a tube cooled to 0° (in which certain hydrocarbons are condensed), and then through a tube surrounded with a freezing mixture, a colourless liquid condenses in the latter, which, when taken out of the freezing mixture, is suddenly converted into a mixture of about equal volumes of butylene and hydride of butyl, the boiling point then rising to about 8° . The less volatile hydrocarbons, which boil from 100° to 300° , exhibited a composition expressed by $C_{24}H_{22}$ or $C_{40}H_{32}$. The butylene is produced from the butylic alcohol, $C_8H_{10}O_2$, by separation of $2HO$; the hydride of butyl, and the less volatile hydrocarbons from the butylene, possibly as represented by the equations—



Butyl, C_8H_9 , the radical of butylic alcohol, is obtained by heating iodide of butyl with potassium in sealed tubes for several days at the temperature of the water-bath. The potassium is gradually converted into iodide: on opening the tubes, butylene gas escapes; and on applying a gentle heat, the vapour of hydride of butyl C_8H_{10} (which may be condensed by a freezing mixture), the boiling point then rising rapidly to 100° . From 105° upwards, butyl, C_8H_9 or $C_{16}H_{18}$, passes over; it is a colourless oily liquid, having a faint odour, and specifically lighter than water.*

	Found.		Calculated.
Carbon . . .	84.26	C_8 . .	84.21
Hydrogen . .	16.15	H_9 . .	15.79
	<hr/> 100.41		<hr/> 100.00

Chloride of Butyl is formed by the action of pentachloride of phosphorus on butylic alcohol; the action is violent, and attended with considerable evolution of heat. The pentachloride is gradually added to the butylic alcohol in a flask having a long neck, which must be kept very cool. The pentachloride is then converted into oxychloride (or the oxychloride may be used in the first instance, in which case the action is less violent). After twenty-four hours, the contents of the flask are distilled off; the portion which distils over below 100° is washed with water, dehydrated with chloride of calcium, and rectified; the portion which goes over below 70° is chloride of butyl. This liquid is lighter than water, and has an ethereal odour, recalling also that of chlorine. It is rapidly decomposed by potassium, with rise of temperature and evolution of gas. Its composition is C_8H_9Cl .

* *Butyl* is identical with the radical formerly described by Kolbe under the name of *Valyl*.

	Found.		Calculated.	
Carbon .	51.21	51.86	C ₈	51.88
Hydrogen	9.69	9.99	H ₉	9.70
Chlorine .	—	—	Cl	38.40
				<hr/> 100.00

Chloride of butyl is also formed by the action of hydrochloric acid on butylic alcohol. When the alcohol is saturated with hydrochloric acid gas, and the liquid enclosed in a sealed glass tube and heated in the water-bath, a large quantity of chloride of butyl is formed, which may be obtained in the separate state by washing the product with water, rectifying it, and collecting apart the portion which distils over between 70° and 75°.

Bromide of Butyl is obtained by adding a few drops of bromine to butylic alcohol, introducing a small quantity of phosphorus after the liquid has cooled to a certain point, and repeating the addition of bromine and the decoloration of the liquid by phosphorus, till vapours of hydrobromic acid are given off in abundance, and a quantity of bromine has been added, at least equal to the butylic alcohol. The liquid is then distilled at a gentle heat not exceeding 100°, whereupon the vapours of hydrobromic acid dissolve in the water, while the bromide of butyl collects at the bottom. This product is washed with water, dried over chloride of calcium, and rectified. Pure bromide of butyl boils at 89°, and smells like chloride of butyl. Its specific gravity at 16° is 1.274. Vapour-density, by experiment, 4.720, while the formula C₈H₉Br gives for a condensation to 4 vols. the number 4.749.

	Found.		Calculated.	
Carbon .	34.58	34.97	C ₈	35.03
Hydrogen	6.79	6.67	H ₉	6.56
Bromine .	—	57.91	Br	58.41
		<hr/> 99.55		<hr/> 100.00

Bromide of butyl is decomposed by potassium very slowly in the cold, but with violence when heated. When the substances were heated together in a sealed tube, the action took place immediately after the fusion of the potassium. Large quantities of gas were evolved, probably butylene and hydride of butyl; and the tube exploded with violence. Ammonia acts but slowly on bromide of butyl at ordinary temperatures, probably with formation of butylamine.

Iodide of Butyl.—Obtained by adding 1.5 pt. iodine to 1 pt. of butylic alcohol, which must be kept cold; gradually introducing about 0.15 phosphorus; and subsequently heating the mixture (at last to

ebullition), the colour of which becomes lighter and brownish-yellow, while hydriodic acid volatilises together with a little iodide of butyl. These vapours are received in cold water; the residue, when cold, washed with this liquid, and afterwards with pure water; then dehydrated by chloride of calcium; and freed from a small quantity of unaltered butylic alcohol, by treating it, while warm, with pulverised iodide of phosphorus* till that compound crystallises out. The liquid then distilled, and the distillate washed with water, dehydrated with chloride of calcium, and rectified, the portion which distils over at 118° to 122° being collected apart. Iodide of butyl recently prepared is a colourless strongly refracting liquid, which, however, soon turns brown when exposed to light. It boils at 121° ; but when a mixture of water and iodide of butyl is distilled, the thermometer at the commencement of the process, when iodide of butyl chiefly distils over, shows a temperature of only 88° to 89° . The specific gravity of iodide of butyl is 1.604 at 19° . Vapour-density by experiment = 6.217: the formula C_4H_9I gives 6.343 for a condensation to 4 volumes.

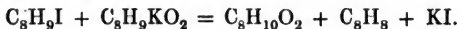
	Found.					Calculated.
Carbon	26.04	26.59	26.26	26.41	—	C_8 26.22
Hydrogen	5.00	5.13	5.04	4.92	—	H_9 4.91
Iodine	—	—	—	—	68.68	I 68.87

Iodide of butyl burns with difficulty, and only in contact with an inflamed body, and gives off vapours of iodine. It is but slowly attacked by aqueous solution of potash, even after long boiling; alcoholic potash decomposes it, with formation of iodide of potassium and butylic alcohol. It is readily decomposed by silver-salts. With an alcoholic solution of nitrate of silver it immediately forms iodide of silver; it likewise acts on dry silver-salts, and this reaction gives rise to the formation of several other ethers from the iodide of butyl.

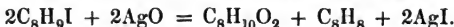
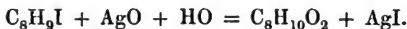
Butylic Ether, C_8H_9O , or $\left. \begin{matrix} C_8H_9 \\ C_8H_9 \end{matrix} \right\} O_2$, is formed by the action of iodide of butyl on the compound $\left. \begin{matrix} C_8H_9 \\ K \end{matrix} \right\} O_2$, produced by the action of potassium on butylic alcohol, but could not be separated by fractional distillation from the excess of butylic alcohol, which boils nearly at the same point. On attempting to remove the excess of butylic alcohol by saturating the liquid with potassium, ultimately with the aid of heat, and treating the still hot liquid with iodide of butyl, a violent

* Wurtz prepares this compound by adding 8 or 10 pts. of iodine to 1 pt. phosphorus in a glass vessel which admits of being closed; violent action takes place, and the resulting compound fuses. The heat is continued for a short time, till the film which adheres to the sides of the vessel becomes dark red and translucent, and the liquid compound separated from the solid phosphorus (which has become amorphous): the compound solidifies in the crystalline state.

action takes place, attended with formation, not of butylic ether, but of butylic alcohol and butylene :



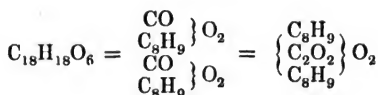
Iodide of butyl is completely decomposed by dry oxide of silver,—with formation of butylic ether and iodide of silver,—the former being, however, associated with small quantities of butylene-gas, water, reproduced butylic alcohol, and carbonate of butyl. The formation of the water and carbonic acid is attributed by Wurtz to the oxidising action of the excess of silver-oxide: the formation of butylic alcohol he regards as taking place in the manner represented by one of the equations :



Vinobutylic Ether, $\text{C}_{12}\text{H}_{14}\text{O}_2 = \left. \begin{matrix} \text{C}_4\text{H}_5 \\ \text{C}_8\text{H}_9 \end{matrix} \right\} \text{O}_2$, is prepared by the action of iodide of ethyl on the compound $\text{C}_8\text{H}_9\text{KO}_2$ at ordinary temperatures. After the mixture had been left to stand for a day, it was distilled, the excess of iodide of ethyl passing over first, then vinobutylic ether, and lastly (above 95°) the excess of butylic alcohol. The last portion of the distillate was again treated with potassium, then the first portion, to form a new portion of vinobutylic ether; and lastly, the entire liquid rectified, the portion which distilled over between 78° and 80° being collected apart. This, which was a colourless liquid having an agreeable odour, exhibited a density of 0.7507, and the composition $\text{C}_{12}\text{H}_{14}\text{O}_2$.

	Found.	Calculated.
Carbon . .	70.15	C_{12} 70.58
Hydrogen . .	14.04	H_{14} 13.72
Oxygen . .	—	O_2 16.70
		<hr/> 100.00

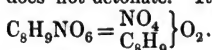
Carbonate of Butyl was prepared by enclosing equal parts of carbonate of silver and iodide of butyl in a sealed glass flask, and heating the mixture in the water-bath for two days. On opening the flask after cooling, a small quantity of carbonic acid escaped, together with a gas (butylene) which burned with a smoky flame. The liquid remaining in the flask was then distilled in the oil-bath, and the portion which passed over above 180° again rectified. Carbonate of butyl thus obtained is a colourless liquid specifically lighter than water, having an agreeable odour like that of carbonate of ethyl, and boiling at 190° . Its composition answers to the formula—



	Found.	Calculated.
Carbon . . .	62.14	C_{18} 62.09
Hydrogen . . .	10.49	H_{18} 10.34
Oxygen . . .	—	O_6 27.67
		<hr/> 100.00

Aqueous ammonia converts it into butylic alcohol and butylic urethane.

Nitrate of Butyl.—Prepared by mixing previously fused nitrate of silver with a small quantity of urea likewise fused, and adding a quantity of iodide of butyl not quite sufficient to decompose the silver-salt; action immediately takes place, and the nitrate of butyl is distilled over, partly by the heat evolved in the reaction, and the rest between 140° and 150° . The distillate, after being washed with water, and dehydrated by chloride of calcium, is a colourless liquid heavier than water, and tasting sweet at first, but afterwards pungent and aromatic. It boils at 130° ; burns with a pale flame; its vapour does not detonate. Its composition corresponds with the formula



	Found.	Calculated.
Carbon . . .	40.55	C_8 40.33
Hydrogen . . .	7.31	H_9 7.56
Nitrogen . . .	—	N 11.76
Oxygen . . .	—	O_6 40.35
		<hr/> 100.00

With alcoholic potash it yields butylic alcohol and nitrate of potash. Sulphuretted hydrogen has no action upon it.

Sulphate of Butyl is formed by the action of iodide of butyl on sulphate of silver at ordinary temperatures. The heat evolved in this reaction is sufficient to exert a decomposing action on the resulting sulphate of butyl; the mixture blackens in separate places; and on opening the vessel in which the action has taken place, the odour of sulphurous acid becomes perceptible. The action may be moderated by cooling the vessel; but the sulphate of butyl is so unstable that it decomposes from one day to another, yielding sulphurous acid, a coloured viscid hydrocarbon, and a peculiar conjugated acid, which may be extracted by treating the residue with water; and forms with baryta a soluble salt which dries up to a gummy mass *in vacuo*.

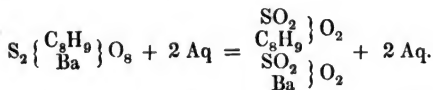
Acetate of Butyl is prepared by decomposing the iodide with nitrate of silver. The latter salt is mixed in a small flask with a nearly equivalent quantity of iodide of butyl, the neck of the flask sealed, and the flask heated for several hours in the water-bath. Iodide of silver is then formed, together with acetate of butyl, which may be separated by distillation. The distillate is washed with water containing a little carbonate of soda in solution, then dried with chloride of calcium, and rectified. Pure acetate of butyl is an ethereal, perfectly colourless liquid, having a very agreeable odour, boiling at 114° , and having a density of 0.8845 at 16° . Vapour-density by experiment = 4.073; by calculation from the formula $C_{12}H_{12}O_4$, 4.017 for a condensation to 4 volumes.

	Found.	Calculated.
Carbon . . .	61.94	C_{12} 62.06
Hydrogen . . .	10.42	H_{12} 10.34
Oxygen . . .	—	O_4 27.60
		<hr/> 100.00

When boiled with solution of caustic potash, it is decomposed with formation of acetic acid and butylic alcohol.

Acetate of butyl may also be obtained by distilling equivalent quantities of sulphobutylate of potash and recently fused acetate of potash. In a similar manner, *Formiate of Butyl* may be prepared: it is a liquid having an agreeable odour, and boiling at about 100° .

Sulphobutyllic Acid may be separated from its baryta-salt by sulphuric acid, but has not yet been minutely examined. The *baryta-salt* is obtained by gradually adding strong sulphuric acid to an equal volume of butylic alcohol, diluting the mixture after twenty-four hours with ten times its volume of water, saturating with carbonate of baryta, and evaporating the filtrate. The baryta-salt crystallises in large white rhombic laminæ which are unctuous to the touch. Their composition is—



	Found.		Calculated.	
Carbon . . .	20.18	—	C_8	20.01
Hydrogen . . .	4.63	—	H_{11}	4.58
Oxygen . . .	—	—	O_3	10.00
Sulphuric acid . . .	—	—	$2SO_3$	33.39
Baryta . . .	31.75	31.73	BaO	32.02
			<hr/>	100.00

The crystals dissolve readily in water : at 100° or *in vacuo* they give off 2 eq. water.

The *potash*-salt of sulphobutylic acid was prepared by diluting the mixture of sulphuric acid and butylic alcohol with twice its bulk of water, mixing it with solid carbonate of potash, evaporating in the water-bath, and exhausting the residue with boiling alcohol. The potash-salt crystallised from the filtrate in broad nacreous laminæ. It dissolves readily in water, with tolerable facility in boiling alcohol, sparingly in cold alcohol. The concentrated aqueous solution is precipitated by alcohol. Its composition is $S_2 \left\{ \begin{smallmatrix} C_8H_9 \\ Ba \end{smallmatrix} \right\} O_8$.

	Found.			Calculated.
Carbon . .	24.82	24.81	C_8	24.97
Hydrogen . .	4.94	—	H_9	6.68
Oxygen . .	—	—	O	—
Sulphuric acid	—	—	$2SO_3$	—
Potash . .	24.11	24.53	KO	24.55

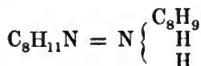
The aqueous solution of this salt distilled with caustic potash, yields butylic alcohol and sulphate of potash.

Sulphobutylate of *lime* was prepared like the preceding salts. By evaporating the aqueous solution, it was obtained in small nacreous crystals, which, under the microscope, presented the appearance of six-sided laminæ. They are anhydrous, dissolve readily in water (the solution is highly efflorescent), and have the composition $S_2 \left\{ \begin{smallmatrix} C_8H_9 \\ Ca \end{smallmatrix} \right\} O_8$; analysis gave 16.41 per cent. lime, while the formula requires 16.18 per cent.

Butylamine.—This base, like all the bases of the series $N \left\{ \begin{smallmatrix} C_nH_{n+1} \\ H_2 \end{smallmatrix} \right\}$ may be obtained by the action of potash on cyanate and cyanurate of butyl. A mixture of these two ethers is obtained by distilling 2 parts of sulphobutylate of potash with 1 part of perfectly dry and recently prepared cyanate of potash. The pasty distillate is dissolved in alcohol, and the solution boiled with addition of fragments of caustic potash. Carbonate of potash is then formed, and butylamine evolved, which is condensed in a small quantity of cold water acidulated with hydrochloric acid. The boiling is continued till the residue is quite fused and no longer gives off alkaline vapours. The resulting solution of hydrochlorate of butylamine is evaporated to dryness, and the salt, after being freed from residual water by fusion, is pulverised when cold, and quickly mixed with an equal weight of quicklime. This mixture is introduced into a tube of hard glass, which must be filled with it to four-fifths. The remaining portion of the tube is filled with

fragments of caustic baryta; a gas-delivery tube bent at right angles attached to this tube, and made to dip into a small flask surrounded with ice; and the tube carefully heated in a combustion-furnace beginning at the closed end. The butylamine which escapes is completely dehydrated by caustic baryta, and condenses in the flask. It boils at 69° to 70° ; smells strongly ammoniacal and somewhat aromatic; is inflammable, and burns with a luminous flame. In contact with hydrochloric acid, it forms dense fumes. It dissolves in all proportions in water or alcohol. The aqueous solution smells like the pure base, and is very caustic; when concentrated, it is somewhat viscid. Most metallic solutions are precipitated by butylamine in the same manner as by ammonia: the precipitates formed in solutions of zinc, cadmium, and copper, dissolve in excess of the precipitant: gelatinous alumina likewise dissolves in excess of butylamine. The oxides of nickel, cadmium, and chromium, do not redissolve in excess of the precipitant. Nitrate of silver forms with butylamine a tawny yellow precipitate easily soluble in excess. Gelatinous silica dissolves very perceptibly in butylamine, and remains in the pulverulent and amorphous state when the solution is evaporated.

The composition of butylamine is expressed by the formula—



	Found.		Calculated.	
Carbon	65.58	65.87	C_8	65.75
Hydrogen	14.99	15.26	H_{11}	15.06
Nitrogen	—	—	N	19.19
				<hr/>
				100.00

Hydrochlorate of butylamine, $\text{C}_8\text{H}_{11}\text{N} \cdot \text{HCl}$, crystallises in deliquescent needles, melts above 100° , emits thick white fumes in the air, and volatilises without residue. It gave by analysis 43.83 per cent. C, and 11.05 H, the formula requiring 43.83 and 10.95.

The platinum salt of butylamine does not separate out immediately on mixing hydrochlorate of butylamine and bichloride of platinum, even in concentrated solutions, but crystallises after evaporation in beautiful orange-yellow laminæ, which are soluble in water and alcohol, and have the composition $\text{C}_8\text{H}_{11}\text{N} \cdot \text{HCl} + \text{PtCl}_2$. Analysis gave 17.18 per cent. C, 4.52 H, and 35.02 Pt, the formula requiring 17.19 C, 4.29 H, and 35.32 Pt.

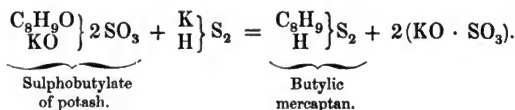
Hydrochlorate of butylamine and terchloride of gold may be mixed without separation of a double salt ; but on evaporating the mixture, the double salt crystallises in yellow rectangular tables, which, when heated above 100° , melt to an orange-yellow liquid. The analysis of these crystals gave 18.79 per cent. C, 4.84 H, and 37.50 Au, the formula $2(\text{C}_8\text{H}_{11}\text{N}, \text{HCl}) + \text{AuCl}_3$ requiring 18.30 C, 4.57 H, and 37.94 Au.

On Butylic Mercaptan and Butylic Urethane.*

By E. Humann.

Butylic Mercaptan, $\text{C}_8\text{H}_{10}\text{S}_2$.—This compound is easily obtained by distilling at the heat of the water-bath a mixture of solution of sulph-hydrate of potassium and a concentrated solution of pure sulphobutylate of potash, taking care to receive the product in a well-cooled flask. The oily liquid which condenses is decanted, placed in contact with chloride of calcium, and then distilled with the thermometer, the portion which distils over between 85° and 95° C. being collected apart.

The reaction which gives rise to the formation of butylic mercaptan is expressed by the following equation :—



Butylic mercaptan thus obtained is a colourless, very mobile liquid, lighter than water, and having the peculiar, disagreeable odour which characterises the mercaptans. Sp. gr. 0.848 at $11^{\circ}5$ C. Vapour-density by experiment, 8.10. Calculation from the formula $\text{C}_8\text{H}_{10}\text{S}_2$ gives 3.11 for a condensation to 4 volumes. Boils at 88° C. Very inflammable, and burns with a very bright blue flame. Very sparingly soluble in water. Mixes in all proportions in alcohol and ether. Has no action on vegetable colours. Dissolves sulphur and iodine.

* Ann. Ch. Phys. [3], xliv. 337.

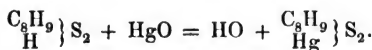
The analysis of this body gave the following results:—

	Experiment.		Calculated.
Carbon .	53·52	53·16	C ₈ 53·33
Hydrogen	11·71	11·32	H ₁₀ 11·11
Sulphur .	—	—	S ₂ 35·56
			<hr/> 100·00

Dilute nitric acid acts very strongly on butylic mercaptan; the liquid becomes red, from formation of a certain quantity of nitric oxide which dissolves in it; but the colour disappears on heating, and an oily liquid is then found on the surface.

Butylic mercaptan, like its homologues, forms compounds in which its basic hydrogen is replaced by a metal. Thus, when it is heated with potassium, hydrogen is evolved, and a white granular substance formed, which is soluble in alcohol, and consists of *butylosulphopotassic alcohol*, $\text{C}_8\text{H}_9\text{K}\text{S}_2$. On pouring an alcoholic solution of butylic mercaptan into acetate of lead, a yellow crystalline precipitate is formed containing $\text{C}_8\text{H}_9\text{Pb}\text{S}_2$.

When an alcoholic solution of butylic mercaptan is poured upon red oxide of mercury, a rapid action takes place, attended with considerable elevation of temperature, and a white substance is formed consisting of *butylomercaptide of mercury*, or *butylosulphomercuric alcohol*:



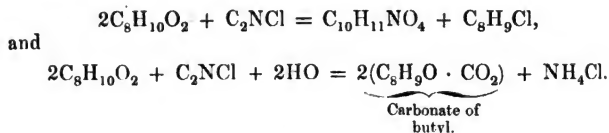
On dissolving the product in boiling alcohol, and leaving the solution to cool, the compound is deposited in white nacreous scales, very fusible, and unctuous to the touch. Their composition is as follows:—

	Expt. (mean).	Theory.
Carbon . . .	25·78	C ₈ 25·39
Hydrogen . . .	5·01	H ₉ 4·76
Mercury . . .	52·55	Hg 52·91
Sulphur . . .	—	S ₂ 16·94
		<hr/> 100·00

This compound is decomposed by sulphuretted hydrogen, yielding sulphide of mercury and butylic alcohol.

Butylic mercaptan acts in a similar manner on other metallic oxides: thus it forms white precipitates with acetate of copper and terchloride of gold.

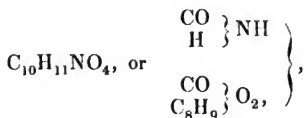
Butylic Urethane, $C_{10}H_{11}NO_4$.—Obtained by the action of gaseous or liquid chloride of cyanogen on butylic alcohol,—its formation being, however, accompanied by that of carbonate of butyl.



The best mode of preparing butylic urethane is to pour liquid chloride of cyanogen into butylic alcohol. The reaction takes place quickly with the aid of heat, more slowly at ordinary temperatures. It is generally indicated by the formation of a mass of crystals within the liquid, in case the butylic alcohol contains a little water. It is complete when the odour of chloride of cyanogen has completely disappeared. The best mode of accelerating it is to heat the mixture in a sealed tube placed in the water-bath. After cooling, the crystals must be well pressed, the liquid introduced into a retort, and distilled. When nearly two-thirds of the liquid has passed over, the receiver is to be changed, and the portion which distils over above $220^\circ C$. collected apart. This product is an oily liquid which solidifies on cooling, and partly collects in the neck of the retort in a shining crystalline mass, which is unctuous to the touch: this is butylic urethane. It must be carefully collected and pressed between folds of blotting-paper. It is finally purified by crystallisation from boiling alcohol.

Butylic urethane thus prepared forms beautiful nacreous scales, which are very brilliant, unctuous to the touch, insoluble in water, soluble in alcohol and ether; they melt at a very gentle heat, and distil without alteration.

The analysis of these crystals gave 51.09 per cent. C, and 9.18 H; corresponding with the formula—



which requires 51.28 C, and 9.40 H.

The first portion of the distillate obtained by the action of chloride of cyanogen on butylic alcohol consists of *Carbonate of Butyl*. On redistilling this liquid, and collecting that which passed over between 180° and 190° C., a colourless, very mobile liquid was obtained, lighter than water, having a very agreeable odour, and yielding by analysis 61.53 per cent. C, and 10.65 H. The formula C_8H_9O, CO_2 , or $C_2O_4 \{ C_8H_9O \}$, requires 62.09 C, and 10.34 H.

Wurtz had previously obtained the carbonate of ethyl by the action of chloride of cyanogen on common alcohol.

On Amylic Alcohol.*

By L. Pasteur.

THE fusel-oil of commerce consists chiefly of a mixture of two kinds of amylic alcohol,—one active, and the other inactive with regard to polarised light. These two varieties are exactly similar in their chemical properties, differ but slightly in density and boiling point, and give rise under similar circumstances to products which resemble each other in all respects, excepting in their relation to polarised light, those which are derived from the active alcohol being themselves active, and those which result from the inactive alcohol being themselves also inactive.

The proportion of the active and inactive alcohols in fusel-oil varies according to its origin: thus the fusel-oil obtained by fermentation of the juice of mangold-wurzel contains about one-third of active, and two-thirds of inactive amylic alcohol, whereas that which is produced by fermentation of the molasses contains about equal parts of the two alcohols. The two alcohols cannot be separated by fractional distillation, but only by fractional crystallisation of the active and inactive sulphamylates of baryta. For this purpose it is necessary to prepare a large quantity of sulphamylate of baryta from crude amylic alcohol rectified by a single distillation in order to free it from water and vinic alcohol. The amylic alcohol thus far purified is mixed, as usual, with an equal weight of sulphuric acid, the mixture treated with carbonate of baryta, then filtered and left to crystallise. The crystals have all the same aspect, lustre, form, and angles; and, as in the case of a perfectly constant and homogeneous substance, the salt may be crystallised either wholly or partially any

* Compt. rend. xli. 296.

number of times, without the slightest change in the aspect of the crystals. Nevertheless the mass is really composed of two kinds of crystals differing in solubility, and in their action on polarised light,—one being, indeed, active, and the other inactive. They are very difficult to separate, in consequence of their complete isomorphism. Nevertheless, the active salt is $2\frac{1}{2}$ times more soluble than the inactive; and if the first crystals which separate be recrystallised about 20 times, a product will at length be obtained which has no action on polarised light; and by repeatedly crystallising the mother-liquor, a solution will ultimately be left containing nothing but the active salt. Lastly, on extracting from these two varieties of the sulphamylate, the amylic alcohol of which they contain the elements, it is found that the more soluble salt yields an amylic alcohol which rotates the plane of polarisation to the left, and to the amount of 20° in a tube 50 centimetres long, while the less soluble salt yields an amylic alcohol which has no perceptible action on polarised light.

The comparative study of these two alcohols exhibits many points of interest. Every reaction that can be performed with the one may likewise be produced with the other, under the same circumstances, and the resemblance of the resulting products often approaches nearly to identity, without ever actually attaining it. Moreover, the active alcohol always gives active products, and the inactive alcohol inactive products, provided we do not go as far as the radical $C_{10}H_{11}$, in which reside the dissymmetry of the molecules and the action on polarised light. One of the most remarkable differences exhibited by the two alcohols is in their densities. The active alcohol is heavier than the other, and the difference amounts to nearly $\frac{1}{1000}$. Consequently, equal volumes of the two alcohols do not contain equal numbers of molecules, those of the active alcohol being more crowded than those of the other; and the difference is considerable for a phenomenon of such a nature. The active alcohol boils at 127° to 128° C., under the ordinary pressure, and the inactive alcohol at 129° . The mixture of the two boils at intermediate temperatures, and not at 132° , as is commonly stated.

On Hypogæic Acid, a new fatty acid obtained from Earthnut-oil.***By A. Gössmann and H. Scheven.**

THE earthnut (*Arachis hypogæa*, L.) is a small, low-growing, leguminous plant, which grows wild in South America and on the south coasts of Africa and Asia, and is cultivated in Italy, Spain, and the South of France. The seeds, which ripen only when the pods are covered up with earth, produce a large quantity of a nearly colourless oil, having an agreeable taste. This oil burns with a bright flame, forms an excellent soap with alkalies, and mixes very readily with essential oils. At $+3^{\circ}\text{C}$. it yields a solid fat resembling stearine, becomes viscid at -3° or -4° , and solidifies completely at -7° .

This oil contains two fatty acids, viz. *Arachinic acid*, belonging to the series $\text{C}_n\text{H}_{2n}\text{O}_4$, and *Hypogæic acid*, belonging to the oleic acid series, $\text{C}_n\text{H}_{2n-2}\text{O}_4$. Arachinic acid was discovered by Gössmann,† who obtained it by saponifying the oil with very strong caustic soda, decomposing the resulting fat with hydrochloric acid, and separating the more solid portion of the fatty acid thus obtained by repeated crystallisation from alcohol and by pressure. After four crystallisations, a solid fatty acid was obtained, exhibiting a constant melting point. It was procured in larger quantity by subjecting the mixed fatty acids to Heintz's method of fractional crystallisation of the lead-salts. Arachinic acid crystallises in very beautiful shiny laminæ; acquires a nacreous lustre by pressure; melts at 75° ; solidifies with radiating structure at 73.5° , and becomes white and like porcelain by keeping. When pure, it dissolves but very sparingly in cold alcohol of ordinary strength, sparingly also in cold absolute alcohol, readily in hot absolute alcohol, and very readily in ether. Its analysis gave the following results:—

Calculated.			Found.			
40 C	240	76.92	76.84	76.84	76.82	—
40 H	40	12.82	12.96	12.93	12.82	12.82
4 O	32	10.26				
<hr/>						
$\text{C}_{40}\text{H}_{40}\text{O}_4$	312	100.00				

The formula was confirmed by the analysis of arachinic ether— $\text{C}_{40} \left\{ \text{C}_4\text{H}_5^{\text{H}_{39}} \right\} \text{O}_4$ prepared in the usual manner by passing hydrochloric acid gas into an alcoholic solution of the acid.

* Ann. Ch. Pharm. xciv. 230.

† Ibid. lxxxix. 1.

Hypogæic acid, $C_{32}N_{30}O_4$, more recently discovered by Gössmann and Scheven, is obtained as follows:—After the earthnut oil had been saponified with caustic soda, and the separated acids purified by repeated fusion in water, they were dissolved in alcohol, precipitated with acetate of magnesia and ammonia, and the liquid filtered. The filtrate was then mixed with an excess of alcoholic solution of acetate of lead and excess of ammonia, and left at rest for several days. As soon as the precipitate ceased to increase, it was collected, dried as quickly as possible by pressure, and thoroughly exhausted with ether in a well-closed cylindrical vessel. The ethereal solution of the lead-salt was then mixed with a slight excess of dilute hydrochloric acid, access of air being as far as possible prevented; the chloride of lead filtered off; and the filtrate several times shaken up with water freed from air by boiling. As soon as the ethereal solution of the oleic acid had become clear, it was taken off and set aside in a well-closed stoppered cylinder till the temperature became favourable for the examination of the acids. The greater part of the ether was then carefully distilled off in the water-bath. As the liquid cooled, an acid crystallised out, which had a slight yellowish colour; but by gentle pressure and recrystallisation from alcohol, it was obtained quite white and in needle-shaped masses. In solution there remained a yellowish acid, which was probably altered by oxidising influences. At a lower temperature, this also crystallised completely in a mass of yellowish stellate, needle-shaped crystals, which by recrystallisation from alcohol were likewise obtained colourless. The several crops of crystals thus purified constitute the new acid—*hypogæic acid*—which is characterised by the following properties.

It consists of colourless acicular aggregates; melts at 34° to 35° C.; dissolves readily in alcohol and ether; saponifies pretty easily even in the cold; becomes yellowish red on exposure to the air, acquiring at the same time an extremely rancid odour, and an acid reaction. The acid, when thus altered, crystallises with great difficulty even at a very low temperature. In this respect it bears some resemblance to ordinary oleic acid.

For analysis, the acid was brought to a constant weight at 100° C. with as little access of air as possible.

Calculated.				Found.		
32 C	. . 192	75.59		75.50	75.68	75.51
30 H	. . 30	11.81		11.70	11.81	11.79
4 O	. . 32	12.60				
<hr/>				<hr/>		
$C_{32}H_{30}O_4$	254	100.00				

Copper-salt, $C_{32}H_{29}Cu_4O_4$.—Prepared by passing an excess of dry ammoniacal gas into an alcoholic solution of the purified acid, and adding an alcoholic solution of acetate of copper. The solution remained clear at first, but when cooled to a low temperature, deposited a fine, light blue, granular, crystallised compound, which, when quickly and carefully dried, remained unaltered, contained no ammonia, and dissolved with tolerable facility in alcohol, forming a clear solution. At $75^\circ C$. it baked together, becoming translucent and waxy. Dried at 100° , it yielded 67·27 per cent. carbon, and 10·40 hydrogen, the formula requiring 67·36 and 10·17.

Baryta-salt, $C_{32}H_{29}BaO_4$.—Obtained, like the copper-salt, in the form of a white granular precipitate, which dissolved when heated, leaving only a small quantity of a very basic salt. The solution on cooling yielded a granular crystalline salt, containing 24·08 per cent. BaO; the formula requires 23·81.

Hypogæic ether, $C_{32} \left\{ C_4H_5^{H_{29}} \right\} O_4$.—This compound was prepared by passing dry hydrochloric acid gas into a solution of the purified acid in 95 per cent. alcohol, as long as it continued to be absorbed; then heating the liquid, leaving it to stand for 24 hours, and repeating the whole process with the layer of ether thus obtained. The product, after being freed from hydrochloric acid by shaking up with water, and from free hypogæic acid by treating it with small quantities of alcohol, was dried in a retort at 100 to 120° in a stream of carbonic acid gas, and analysed.

Calculated.				Found.		
36 C	. .	216	76·59	76·56	76·91	76·72
34 H	. .	34	12·05	12·01	11·92	11·93
4 O	. .	32	11·36			
		<hr/>	<hr/>			
		282	100·00			

Hypogæic ether has a yellowish colour, probably arising from slight impurity; it is not volatile, heavier than alcohol (at the bottom of which it collects), lighter than water. It is insoluble in water, and dissolves very sparingly in alcohol, whence the latter is well adapted to free it from unetherised acid.

The authors endeavoured also to ascertain whether the earthnut-oil contains any other acid of the oleic series besides hypogæic acid. For this purpose, the entire quantity of acid separated from the ethereal

solution of the lead-salt obtained from a certain portion of the oil was converted into ether, and the ether analysed. This ether gave quantities of carbon and hydrogen agreeing exactly with the above; hence, as the lead-salts of all the acids of the oleic series are soluble in ether, it may be concluded that no other acid of that series is contained in the oil.

On Papaverine.*

By T. Anderson.

IN the mother-liquors obtained in the purification of narcotine by repeated crystallisation from boiling alcohol, Anderson has found, besides narcotine, the more soluble alkaloid papaverine. This body is obtained free from narcotine by finely pulverising the last crystals obtained from the mother-liquors, and digesting the powder with a small quantity of acetic acid, which then combines only with the papaverine. As soon as the liquid becomes neutral, it is decanted, the residue again treated with a small quantity of acetic acid, and this treatment repeated as long as the acetic acid is completely neutralised by contact with the residue. From the liquid filtered from the undissolved narcotine, the papaverine was precipitated by ammonia and recrystallised from boiling alcohol. Papaverine was obtained in considerable quantity from the mother-liquor remaining after the first crystallisation of the crude narcotine, by precipitating that liquid with subacetate of lead; boiling the finely pulverised precipitate with alcohol; driving off the alcohol from the dark alcoholic decoction; treating the residue with dilute hydrochloric acid; concentrating the hydrochloric acid solution of narcotine and papaverine filtered from the black resinous matter; removing from the liquid the crystals of the sparingly soluble hydrochlorate of papaverine, which separate in a few days; purifying them by repeated recrystallisation; separating out the base by means of ammonia; and purifying it by recrystallisation from boiling alcohol. The analysis of the product thus obtained exhibited the composition found by Merck,† viz. $C_{40}H_{21}NO_8$.

* Ed. Phil. Trans. xxi. Pt. 1; Ann. Ch. Pharm. xciv. 235.

† Ann. Ch. Pharm. lxxiii. 50.

	Found.			Calculated.	
Carbon .	70.71	70.60	70.58	C ₄₀	70.79
Hydrogen	6.29	6.46	6.46	H ₂₁	6.20
Nitrogen*	4.40	3.96	—	N	4.14
Oxygen .	18.60	18.96	—	O ₈	18.78

The platinum-salt gave 17.82 per cent. platinum, the calculated quantity being 18.10.

Action of Nitric Acid.—Papaverine dissolves in dilute nitric acid without decomposition; but on mixing the solution with an excess, especially of strong nitric acid, and heating the liquid, a vivid action takes place; red fumes are evolved; the liquid assumes a deep red colour; and orange-coloured crystals separate out from it, consisting of the nitrate of a new base, *Nitropapaverine*. This base separates from a solution of the salt in boiling water or in excess of nitric acid, on addition of ammonia, in the form of a light yellow flocculent precipitate, and after recrystallisation from boiling alcohol is obtained in needles. It is insoluble in water, soluble in alcohol and ether, blues reddened litmus paper, dissolves in acids, and neutralises them completely, forming salts which are all of a pale reddish yellow colour, and insoluble in water. It fuses when heated, and burns away quickly at a higher temperature. When boiled with strong solution of potash, it gives off traces of a volatile base. It does not, like papaverine, give a purple colouration with sulphuric acid. Its composition is $C_{40}H_{20}(NO_4)NO_8$.

	Calculated.	Found.
40 C . . .	240	62.50
20 H . . .	20	5.20
2 N . . .	28	7.29
12 O . . .	96	25.01
	<hr/> 384	<hr/> 100.00

The crystals which separate from the alcoholic solution retain 1 eq. of water (2.29 per cent.)

The nitrate of nitropapaverine prepared as above forms four-sided

* Anderson observes that papaverine precipitated by ammonia appears to carry some of the ammonia down with it, which makes the nitrogen determination come out too high. The second of the above determinations of nitrogen was made with papaverine which had been precipitated by potash.

tables generally of an orange colour, but yellow when quite pure. The crystals are anhydrous. It is nearly insoluble in cold, somewhat more soluble in boiling water, and dissolves abundantly in water mixed with nitric or hydrochloric acid; dissolves also in alcohol and ether. When heated, it melts and burns quickly away, leaving a black substance, which also burns completely away at a stronger heat. Its composition is $C_{40}H_{20}(NO_4)NO_8 \cdot HO \cdot NO_5$.

	Found.		Calculated.
Carbon . .	53·68	C_{40} . .	53·69
Hydrogen . .	4·95	H_{21} . .	4·69
Nitrogen . .	—	N_3 . .	9·38
Oxygen . .	—	O_{18} . .	32·24
<hr/>			
			100·00

Sulphate of nitropapaverine dissolves sparingly in water, and crystallises in small prisms.

Hydrochlorate of nitropapaverine likewise dissolves but sparingly in water, but readily in excess of hydrochloric acid, and in alcohol; it crystallises in pale yellow needles. Bichloride of platinum added to its solution throws down the platinum-salt, $C_{40}H_{20}(NO_4)NO_8HCl \cdot PtCl_2$ in the form of a pale yellow precipitate.

	Found.		Calculated.
Carbon . .	40·47	C_{40} . .	40·66
Hydrogen . .	3·80	H_{21} . .	3·55
Nitrogen . .	—	N_2 . .	4·72
Oxygen . .	—	O_{12} . .	16·26
Chlorine . .	—	Cl_3 . .	18·09
Platinum . .	16·56	Pt . .	16·72
<hr/>			
			100·00

Action of Bromine.—When bromine-water is added by drops to a solution of hydrochlorate of papaverine, a precipitate is formed which redissolves at first, but afterwards remains permanent; this precipitate is the hydrobromate of *Bromopapaverine*. From this salt, the base itself is readily obtained by digestion with ammonia and recrystallisation from boiling alcohol; as the solution cools, the base separates in small white needles, which are insoluble in water, but readily soluble in alcohol and ether. The crystallised base is anhydrous, and its composition $C_{40}H_{20}BrNO_8$.

	Found.		Calculated.
Carbon . .	57.23	C_{40} . .	57.41
Hydrogen . .	5.02	H_{20} . .	4.78
Nitrogen . .	—	N . .	3.34
Oxygen . .	—	O_8 . .	15.34
Bromine . .	19.45	Br . .	19.13
		<hr/>	
		100.00	

The hydrobromate is obtained, as above mentioned, from the concentrated liquid, as a yellowish, but from a more dilute solution as a white precipitate; from the solution in boiling alcohol, it separates in the form of a crystalline powder; it is insoluble in water. When heated, it melts and decomposes. Its composition is $C_{20}H_{20}BrNO_8 \cdot HBr$.

	Found.		Calculated.
Carbon . .	48.36	C_{40} . .	48.09
Hydrogen . .	4.35	H_{21} . .	4.20
Nitrogen . .	—	N . .	2.80
Oxygen . .	—	O_8 . .	12.85
Bromine . .	32.48	Br_2 . .	32.06
		<hr/>	
		100.00	

Hydrochlorate of bromopapaverine dissolves, though sparingly, in water.

Action of Chlorine.—When chlorine gas is passed into a solution of hydrochlorate of papaverine, the liquid becomes brown, and after a while deposits a dingy grey precipitate, which is insoluble in water, but dissolves in boiling alcohol, and separates from that solution in the form of a resin. Ammonia withdraws hydrochloric acid from it, and leaves undissolved a pulverulent substance, which is a basic chlorinated substitution-product.

Action of Iodine.—An alcoholic solution of papaverine mixed with tincture of iodine, yields after a while small crystals, which, when recrystallised from boiling alcohol, form rectangular prisms, having a purple-red colour by reflected, and dark red by transmitted light. They are insoluble in water, are not attacked by dilute acids, but are quickly decomposed by ammonia and potash, papaverine then remaining. Their composition is $C_{40}H_{21}NO_8 + 3I$. When the liquid separated from these crystals is evaporated, another compound separates out, which, after recrystallisation from alcohol, forms thin needles, exhibiting an orange-colour by transmitted light, but leaving

a reddish surface. This compound remains unaltered at 100° , but gives off iodine at a higher temperature. Its composition is



	$\text{C}_{40}\text{H}_{21}\text{NO}_8 + 3 \text{I}.$		$\text{C}_{40}\text{H}_{21}\text{NO}_8 + 5 \text{I}.$	
	Found.	Calculated.	Found.	Calculated.
Carbon . .	33.02	33.47	24.78	24.76
Hydrogen . .	3.21	2.92	2.59	2.16
Nitrogen . .	—	1.95	—	1.44
Oxygen . .	—	8.95	—	6.63
Iodine . .	52.90	52.71	64.60	65.01
	100.00		100.00	

Action of Soda-lime.—When papaverine is heated with four times its weight of soda-lime, a volatile base is evolved, the platinum salt of which contains 36.21 per cent. of platinum, a result intermediate between the quantities of platinum in the corresponding salts of propylamine and ethylamine. Anderson thinks it probable that both these bases were present.

On the Volatile Bromine-compound obtained in the Technical Preparation of Bromine.*

By M. Hermann.

IN the preparation of bromine from the last portions of the mother-liquor obtained from the Schönebeck salt-spring,† there distils over, together with the free bromine, an oily liquid, which, being less volatile than bromine itself, remains in the first of the series of receivers used to condense the products. This substance was formerly regarded by Hermann as a definite compound C_2HBr_2 , the variations in its boiling point being attributed to the facility with which it decomposes; but later experiments, performed with a larger quantity of material, have shown that this view is incorrect, and moreover that the liquid cannot be brought to a definite state by fractional distillation, even in an atmosphere of carbonic acid. By subjecting the

* Ann. Ch. Pharm. xcv. 211.

† J. pr. Chem. lx. 5.

liquid, however, to the following treatment, a definite compound is obtained from it.

The oily liquid cooled to -20°C . by a mixture of ice and salt, solidifies for the most part in white shining crystalline laminae. To purify these, the mother-liquor is carefully decanted, the crystals melted, again crystallised and separated from the mother-liquor, and these operations several times repeated. The solidified mass, after being freed as completely as possible from the mother-liquor, is then introduced into a capacious funnel, in the apex of which is placed a small perforated filter. At first the principal part of the mother-liquor runs off, and the rest is displaced by the liquid proceeding from the gradually melting crystals. The product which last drips from the melting crystals may be regarded as perfectly pure. If the mother-liquor obtained as above be again treated in the same manner, a product is ultimately obtained which no longer crystallises at -20°C .

The melting point of the crystals is -9°C . : if they have previously been completely dehydrated by remaining some time over dry chloride of calcium, they form in the melted state a colourless, very mobile liquid, having a saccharine taste, with a very persistent burning aftertaste. When exposed to the air, they decompose to a certain extent, assuming a red colour, from the presence of free bromine. When distilled even in a stream of carbonic acid, they are decomposed in the same manner as the crude liquid, a small quantity of the above-mentioned bromide of carbon being ultimately formed. When exposed to the action of chlorine in sunshine, the liquid is gradually but completely converted into solid chloride of carbon.

The analysis of the crystals gave the following results :—

		Calculation.	Expt. (mean).
2 C	12	4.74	4.80
H	1	0.40	0.43
3 Br	240	94.86	94.77
<hr/> C ₂ HBr ₃		<hr/>	<hr/>
	253	100.00	100.00

The substance appears, therefore, to be *Bromoform* ; in fact, it agreed perfectly in composition and properties with a sample of that compound prepared in the ordinary way. Its formation is due to the action of the free bromine on the highly carboniferous organic matters contained in the mother-liquor of the salt-spring.

It is generally supposed that bromoform, like chloroform, is converted by caustic potash into bromide of potassium and formiate of potash. This, however, is not the case. Not a trace of formic acid

is produced, and the reaction is different according as the hydrate of potash is used in the free state, or dissolved in alcohol.

When hydrate of potash is brought in contact with bromoform, no action takes place at first, but after a while the mass becomes so strongly heated that the bromoform begins to distil over, and at the same time a gas is evolved, which, when freed by agitation with water from a small quantity of diffused bromoform, exhibits the characters and composition of pure carbonic oxide. The decomposition is expressed by the following equation :—



and is analogous to that which the corresponding oxygen-compound, viz. formic acid, undergoes under the influence of sulphuric acid.

With an alcoholic solution of potash, on the other hand, the evolved gas is a mixture of carbonic oxide and olefiant gas, the latter proceeding from the alcohol, which, under these circumstances, is resolved into olefiant gas and water, its decomposition being induced by that of the bromoform. The relative quantities of carbonic acid and olefiant gas thus produced, vary with the degree of concentration of the alcoholic solution of potash ; but it is especially remarkable that the simultaneous decompositions of the bromoform and alcohol, though not connected by any mutual action, nevertheless take place in simple atomic proportions : so that, for example, 1 atom alcohol is decomposed for every 3 atoms bromoform ; or, with a differently concentrated solution, 5 atoms bromoform to 3 atoms alcohol ; thus affording an example of the remarkable law discovered by Bunsen relating to the coefficients of affinity.

The non-crystallisable portion of the original liquid appears to contain protobromide of carbon, C_2Br_2 .

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XII.—*On the Volatile Oil of "Ptychotis Ajwan."*

By R. HAINES, M.B.,

PROFESSOR OF MATERIA MEDICA IN THE GRANT MEDICAL COLLEGE, BOMBAY.

THIS umbelliferous plant grows abundantly in Rajpootana and in various other parts of Central India. The fruit is short, compressed laterally; and in shape, size, and appearance, very closely resembles that of *Conium maculatum*. It has a powerful and agreeable odour of thyme. The process of extracting its volatile oil is well known to the natives, and is practised pretty extensively in the state of Judore and the neighbouring territories. The oil is used by the native doctors as a carminative, under the name of *Ajwa ke tel*, or Ajwa oil. This, as sold in the Bombay bazaars, is of a dark amber-yellow colour, somewhat viscid, and not pouring freely, as if loaded with resin or fixed oil. It has a pure odour of thyme.

Redistilled with water, it yielded, after cohobating the water several times, a little more than one-fourth of its bulk of a limpid bright yellow oil. The residue was a dark orange-yellow, viscid, oily liquid, almost free from odour.

This residue was sparingly soluble in alcohol, even when boiling, and itself dissolved an appreciable quantity of alcohol. On evaporating the alcoholic solution, the oil was obtained unchanged in its properties. It did not appear to contain resin. It was more soluble in ether. Boiled with potash it formed a soluble soap. Under a heat gradually increasing to near redness, it was converted into volatile

liquid and gaseous products, giving off the pungent odour of acrolein. A small residue of carbon was left in the retort. Warmed with solution of pernitrate of mercury, it did not solidify or undergo any material change, beyond becoming of a darker colour and somewhat more viscid. It consisted, therefore, essentially of a siccative fixed oil,—probably poppy oil,—with which the volatile oil had been adulterated.

The rectified oil, distilled by itself, began to boil at 350° F., the boiling point slowly rose to 366°, at which about one-third came over, and then advanced more rapidly to 450°. A small dark-coloured residue was left in the retort.

The product by repeated fractional distillation was separated into two portions, one boiling at 353°, the other at 440°—450°; the former amounting to about two-thirds, the latter to one-third of the whole.

The more volatile portion was colourless, refracted light strongly, and had a peculiar, sweetish, smoky odour, reminding somewhat of caraway, but entirely distinct from that of thyme. Digested over powdered chloride of calcium, and re-distilled, it retained the same boiling point. Re-distilled over hydrate of soda, its boiling point was reduced to 347°, at which it remained constant. Its specific gravity at 80° was 0·845.

Burnt with oxide of copper, the following results were obtained:—

- I. 6·69 grains gave 6·43 water.
 II. 8·62 " " 8·20 " and 28·51 carbonic acid.
 III. 7·59 " " 7·35 " " 24·92 " "

Calculated.			Found.		
			I.	II.	III.
20 C	120	89·55	—	90·20	89·54
14 H	14	10·45	10·68	10·57	10·76
	134	100·00		100·77	100·30

It is, therefore, isomeric if not identical with cymole— $C_{20}H_{14}$.

The portion which boiled at 440°—450° had a yellowish colour, which could not be removed by repeated distillation. Its odour was that of the original oil, but more concentrated. When kept for several days, it did not crystallise; but on throwing into it a minute fragment of the stearoptene previously deposited from the oil, crystals began to form immediately, and in a few hours it had become almost wholly converted into nearly colourless crystals, forming flattish

tables of a rhomboidal shape, surrounded by a dark yellow oily liquid. By pressure between folds of blotting paper, the crystals were obtained dry and pure.

They were then found to be identical with the crystals sold in the bazaar as *Ajwa ka phul*, or flowers of Ajwa.* They have a powerful odour of thyme, and a hot and very pungent taste; are insoluble in water, but freely soluble in alcohol, ether, and volatile oils. At 127° F. they melt to a colourless liquid, which begins to boil at 439°; but the temperature quickly rises to 447°, at which the whole comes over. The distilled liquid is colourless, not so strongly refractive as the more volatile liquid, and it may be kept for weeks in closed vessels in a fluid state, until a fragment, however minute, of its crystal is thrown in, when crystallisation instantly begins in all directions throughout the liquid. The latter was neutral to test-paper. Its specific gravity at 78° was 0·939.

Sulphuric acid combines with it without charring, forming a colourless or pinkish crystalline mass, soluble in water and yielding a soluble salt with baryta.

Nitric acid, aided by heat, oxidises it rapidly, and gives rise to the production of a gamboge-yellow, sticky resin.

A crystal thrown into nitro-muriatic acid causes the instant formation of a dark green colour, which passes after a few minutes into brown, with the formation of a resin.

It did not combine with hydrate of soda, or with a strong solution of potassa. Heated with solid potassa, it yielded no ammonia.

It was analysed by combustion with oxide of copper.

- I. 5·31 grains yielded 4·57 of water. (The carbonic acid was lost.)
 II. 5·73 " " 4·93 " and 16·75 of carbonic acid.
 III. 6·67 " " 5·72 " 19·43 " "

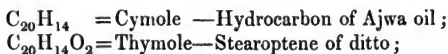
Its composition is, therefore, as follows :—

Calculated.			Found.		
			I.	II.	III.
20 C	120	80·00	—	79·72	79·45
14 H	14	9·33	9·56	9·56	9·53
2 O	16	10·67	—	10·72	10·02
	150	100·00		100·00	100·00

* I have not been able to discover by what method the natives contrive to obtain the stearoptene from the oil: it is probably so loaded with it as to crystallise out on dropping in a fragment ready formed, without its being necessary to re-distil the oil.

It is evidently, therefore, identical with the stearoptene of the oil of thyme, or thymole, described by M. Lallemant in the *Comptes rendus* of Sept. 26th, 1853. I could not observe, however, the property which M. Lallemant assigns to thymole,—of combining with caustic alkalies. The reaction with nitro-muriatic acid is also, I believe, new.

Oil of Ajwa, then, combines the properties of the oils of cumin and thyme, having the hydrocarbon of the one, and the oxidised oil of the other, thus :—



and it thus presents an exception to the general relation of the components of volatile oils, the stearoptene being simply the hydrocarbon *plus* oxygen, without the separation of any portion of the hydrogen.

XIII.—On Azobenzole and Benzidine.

By ALFRED NOBLE,

ASSISTANT IN THE ROYAL COLLEGE OF CHEMISTRY.

WHILE converting nitrobenzole into aniline by M. A. Béchamp's modification of Zinin's process, I observed a few facts, which I beg permission to lay before the Chemical Society.

M. Béchamp's process consists in reducing the nitrobenzole by a mixture of iron filings and acetic acid; and his method is remarkable for the facility with which the conversion of the nitrobenzole is effected,—the former method, as chemists will recollect, being slow and extremely imperfect. The proportions recommended by M. Béchamp* are 2 parts of nitrobenzole, 2 parts of acetic acid, and 3 parts of iron filings. In an experiment in which the amount of iron was considerably increased above the proportions indicated, I found that the result of the operation materially differed from what M. Béchamp had observed. The first portion of the distillate, as in M. Béchamp's process, consisted essentially of aniline, mixed

* Ann. Ch. Phys. xlii.

with a small amount of nitrobenzole which had escaped decomposition; whilst the last product,—about one-third of the whole,—was a liquid of a deep red colour, which solidified in the neck of the retort and in the condenser-tube into a beautifully crystalline compound.

The results of several repetitions of this operation satisfied me that the largest quantity of this substance was obtained if the amount of iron employed was double that recommended by M. Béchamp, viz. 3 parts of iron to 1 of nitrobenzole and 1 of acetic acid.

This red crystalline substance was purified by washing, first with HCl (to separate any adhering aniline), then with water, and afterwards dissolving in boiling alcohol, when, on cooling, yellowish-red crystalline plates were deposited. These crystals were recrystallised once more from alcohol, and dried in the water-bath, at which temperature they fused: their composition was determined by a combustion with oxide of copper.

0.26 grm. of substance gave :

0.755 grm. of CO_2 , and 0.134 grm. of HO.

These numbers lead to the formula of azobenzole, $\text{C}_{12}\text{H}_5\text{N}$, as may be seen from the following comparison of the theoretical and experimental numbers :—

		Theory.		Experiment.
		Equivalent.	Percentage.	
C_{12}	.	72	79.12	79.19
H_5	.	5	5.49	5.69
N	.	14	15.39	—
		<hr/> 91	<hr/> 100.00	

Perfectly pure azobenzole may be obtained in this manner with greater facility than by any other process.

A portion of azobenzole obtained by the above method was converted into benzidine by Zinin's well-known process, viz. by treating an alcoholic solution of this substance with ammonia and sulphuretted hydrogen. An analysis of the platinum-salt of the base thus obtained furnished an additional proof of the identity of the substance obtained as described above, with azobenzole.

0.268 grm. of platinum-salt gave :

0.088 grm. of platinum = 32.88 per cent. of Pt.

The formula $C_{12}H_6N, HCl, Pt Cl_2$ requires 33·09 per cent. of platinum.

Benzidine exhibits a very interesting deportment with nitrous acid: when it is gently heated in the gas of this acid, as obtained by treating starch with nitric acid, a powerful reaction is observed. The substance assumes an orange-red colour, and exhibits, after being treated with water and crystallised from alcohol, all the properties of azobenzole.

The fact of the reproduction of this body from benzidine was, moreover, established by a combustion which furnished the following numbers:—

0·215 grm. of substance gave :
0·623 grm. of CO_2 , and 0·112 grm. of HO .

Theory.			
	Equivalent.	Percentage.	Experiment.
C_{12} . .	72	79·12	79·02
H_5 . .	5	5·49	5·78
N . .	14	15·39	—
	<hr/> 91	<hr/> 100·00	

The simplest formulæ for azobenzole and benzidine only differ by 1 equivalent of hydrogen—

Azobenzole	$C_{12}H_5N$
Benzidine	$C_{12}H_6N$

—a relation which sufficiently explains the transformation and reproduction of azobenzole.

XIV.—*A Few Notes on Barium.*

By A. MATTHIESSEN, Ph.D.

IN continuing my researches in Professor Bunsen's laboratory on the electrolytical separation of the metals of the alkalies and alkaline earths, it has not been possible for me to obtain barium in a regulus

after the same manner in which strontium and calcium have been isolated, but I have invariably separated it in the form of a finely-divided powder. The reason of this appears to be, that at the temperature at which the chloride fuses, the metal attacks the pipe-stem, and decomposes small quantities of alumina and silica, at the same time forming baryta, which prevents the powder melting together. As the iodides, bromides, and fluorides are either infusible, or only fuse at a temperature where the same circumstances hinder the powder from melting together, it does not seem probable that barium can be obtained in a regulus electrolytically, like calcium or strontium. The barium powder has a yellow colour like strontium, decomposes water at ordinary temperatures, and oxidises quickly when exposed to the atmosphere. If, at the negative pole, a platinum wire be used in lieu of the iron one, and the electrolysis be conducted otherwise in the same manner as in the separation of strontium, an alloy of platinum with barium will be formed. This alloy, like those of calcium and strontium, possesses a yellow colour, is very brittle, and decomposes water slowly at ordinary temperatures, leaving the platinum in a finely-divided state.

On the Hydro-electric Currents generated by Couples formed of Single Metals.

By Richard Adie.

THE mode of experimenting was as follows:—Two square pieces of the same metal, having an area varying from one-fourth to one-tenth of a square inch (the preference being ultimately given to small plates), were connected with a delicate galvanometer by means of narrow strips partly cut from one of their edges, and turned vertically upwards. They were then cemented down to a flat plate, so as to expose only one of their surfaces, and sufficient water poured on to cover them. An acid liquid was then poured, by means of a pipette, over one of the plates, and its effect on the galvanometer noted.

The general results of the experiments are given in the following table, in which the word *positive* or *negative* denotes the state of the metal on which the acid was poured:—

		Hydrochloric Acid.	Sulphuric Acid.	Nitric Acid.	Nitro- Hydrochloric Acid.
Platinum no decided action	negative feebly	negative feebly	negative feebly	negative
Palladium positive	positive feebly	positive feebly	negative	positive
Gold negative feebly	negative	negative	negative	negative
Aluminum positive	no action	negative	negative	positive
Silver positive	positive	negative	negative	positive
Antimony positive	negative feebly	negative	negative	positive
Bismuth positive	positive	negative	negative	positive
Copper positive	positive feebly	negative	negative	positive
Cobalt positive	positive feebly	negative	negative	negative
Nickel positive	positive	negative	negative	positive
Arsenic positive	positive feebly	negative	negative	negative
Mercury positive	negative	negative	negative	positive
Cadmium positive	positive	negative	negative	positive
Zinc positive	positive	negative	negative	positive
Lead positive	positive	negative	negative	positive
Tin positive	positive	positive	positive	positive
Tin, Protosulphuret of	positive	no action	negative	negative	positive feebly
Iron negative	negative	negative	negative	negative
Iron, Carburet of, or					
Black-lead positive feebly	negative feebly	negative	negative	negative
Iron, Protosulphuret of	negative	negative	negative	negative	negative

Specific gravities of the acids used :—Hydrochloric, 1.150 ; nitric, 1.402 ; sulphuric, 1.690.

PROCEEDINGS
AT THE
MEETINGS OF THE CHEMICAL SOCIETY.

November 5, 1855.

Dr. W. A. MILLER, President, in the Chair.

The following donations were announced:—

Specimens of Graphite: from the late Mr. Brockedon.

A specimen of Lithium: from Dr. Matthiessen.

“The Journal of the Society of Arts,” from June to November: from the Society.

“The Journal of the Photographic Society,” from June to November: from the Society.

“The Pharmaceutical Journal,” from June to November: from the Editor.

“The Literary Gazette,” from June to November: from the Publishers.

“Notices of Meeting of the Royal Institution:” from the Institution.

“List of Members and Officers of the Royal Institution:” from the Institution.

“Proceedings of the Liverpool Literary and Philosophical Society, 1854–55:” from the Society.

“The Proceedings of the Royal Society,” Nos. 14 and 15: from the Society.

“On the Chemical Composition of Mineral Charcoal:” by T. H. Rowney, Ph.D.

“Researches on the Amides of the Fatty Acids:” by T. H. Rowney, Ph.D.

“On Adipocire and its Formation:” by Charles M. Wetherill, Ph.D., M.D.

- "The Relations of Science:" by John M. Ashley.
- "The Journal of the Franklin Institute," Nos. 355, 356, and 357 : from the Institute.
- "Eighth and Ninth Annual Reports of the Board of Regents of the Smithsonian Institution."
- "Proceedings of the American Philosophical Society for 1854."
- "The American Journal of Science and Art," July and September : from the Editors.
- "Smithsonian Contributions to Knowledge," Vol. 7.
- "Smithsonian Report, 1854."
- "Constitution and By-Laws of the New Orleans Academy of Sciences."
- "Proceedings of the New Orleans Academy of Sciences," Vol. 1, No. 1, March 1854.
- "Ofversicht af Kongl. Vetenskaps Akademias Förhandlingar ; Stockholm, 1854."
- "Jahrbuch der geologischen Reichsanstalt zu Wien, 1854."
- "Jahrbücher der Central-Anstalt für Meteorologie und Erdmagnetismus, von Karl Kreil, Wien : " Vol. 3, 1855. Wien.
- "Denkschriften der Kaiserlichen Akademie der Wissenschaften," Vols. 8 and 9.
- "Sitzungsberichte der Kaiserlichen Akademie der Wissenschaften," Vols. 14 and 15, and Part 1 of Vol. 16.
- "Bulletins des Sciences de l'Académie royale." Brussels, 1855.
- "Annuaire de l'Académie royale des Sciences." Brussels, 1855.
- "Bulletin de la Société Vaudoise des Sciences Naturelles."
- "Sur la Relation entre la Température et la Durée de la Végétation des Plantes," par Quetelet.

Constant A. Sanceau, Professor of Chemistry, of West House, Southshare, near Blackpool, Lancashire, was duly elected a Fellow of the Society.

The following papers were read :—

- "A few Notes on Barium:" by A. Matthiessen, Ph.D.
- "On the Hydro-electrical Currents generated by Couples formed of Single Metals:" by Richard Adie, of Liverpool.

November 19, 1855.

R. PORRETT, Esq., Treasurer, in the Chair.

George F. Wilson, Esq., of Belmont, Vauxhall, was duly elected a Fellow of the Society.

The following papers were read :—

“ On the Volatile Oil of ‘ *Ptychotis Ajwan*’ :” by R. Haines, M.B., Professor of Materia Medica in the Grant Medical College, Bombay.

“ On the Action of Light upon Chloride of Silver :” by F. Guthrie, Ph.D.

December 3, 1855.

Dr. W. A. MILLER, President, in the Chair.

The following donations were announced :—

“ The Journal of the Society of Arts :” from the Society.

“ The Journal of the Photographic Society :” from the Society.

“ The Literary Gazette :” from the Publishers.

“ The Pharmaceutical Journal :” from the Editor.

“ The Quarterly Journal of the Geographical Society :” from the Society.

A specimen of Glycerine produced in the preparation of lead-plaster, having a sp. gr. 1·2 : presented by Mr. G. Whipple.

The following papers were read :—

“ On Azobenzole and Benzidine :” by Mr. Alfred Noble, Assistant in the Royal College of Chemistry.

“ Note on the Detection of Silver in Stains caused by Nitrate of Silver on the Human Skin :” by T. E. Mayer, of Madras.

“ On Insolinic Acid :” by A. W. Hofmann.

December 17, 1855.

Dr. W. A. MILLER, President, in the Chair.

The following donations were announced :—

“The Journal of the Franklin Institute :” from the Institute.

“The American Journal of Science and Art :” from the Publishers.

“The Journal of the Society of Arts :” from the Society.

“The Literary Gazette :” from the Publishers.

A pamphlet, “On two new Crystalline Compounds of Zinc and Antimony,” by J. P. Cooke, jun. : from the Author.

A paper was read :—

“On the Analysis of some of the Grains commonly used as Food by the Native Inhabitants of Southern India :” by J. E. Mayer, of Madras.

NOTICES
OF
PAPERS CONTAINED IN OTHER JOURNALS.

BY HENRY WATTS, B.A., F.C.S.

On Coumaramine, a new Organic Base derived from Nitrocoumarine.*

By A. Frapolli and L. Chiozza.

BLEIBTREU, in his research on coumarine,† mentions some experiments made for the purpose of decomposing nitrocoumarine. The product which he obtained by treating an alcoholic solution of nitrocoumarine with sulphide of ammonium, was uncrystallisable, dissolved in ammonia, and gave with lead and silver salts, precipitates containing sulphur. The action of other ordinary reducing agents likewise fails to yield any simple and definite result. Hydrogen in the nascent state, as evolved from a solution of nitrocoumarine in potash, has no action on that body; neither is any reducing action exerted by hypophosphite of potash or ammonia. The only process by which the authors have been able to effect the reduction of nitrocoumarine consists in the employment of ferrous acetate,—a body whose advantages as a reducing agent have been already pointed out by Béchamp.‡

When nitrocoumarine is introduced into a mixture of acetic acid and iron filings, and the liquid heated in the water-bath, action soon takes place; ferric oxide separates out in considerable quantity; and, as the mixture cools, yellow needles are deposited on the sides of the vessel. To render the action complete, the substances must be left in contact for twenty-four hours. The precipitated ferric oxide is then filtered from the solution of ferrous acetate, the solution concentrated by evaporation, repeatedly filtered hot during the evaporation, to separate the ferric oxide which is continually forming, and then left to cool. It then deposits yellow crystalline needles of an organic base, which the authors designate by the name *Coumaramine*.

Alcohol extracts from the precipitate an additional quantity of

* Ann. Ch. Pharm. xcv. 252.

† Ibid. lix. 177.

‡ Ibid. xcii. 401.

coumaramine, which may be purified by evaporating the alcoholic solution in the water-bath, and re-dissolving the residue in water. This second aqueous solution is to be treated like the first. During the concentration and filtration of the aqueous solutions, part of the coumaramine appears to be decomposed, and the crystals obtained from such a solution are always contaminated with an amorphous brown precipitate.

The crystals which first separated were purified by repeated crystallisation from water; they then formed beautiful prismatic needles of reddish-yellow colour. When a few grammes of substance are used, crystals 6 or 8 centimetres long may be readily obtained. These crystals dissolve but very sparingly in cold water, but appear to be more easily soluble in a saturated solution of ferrous acetate. Boiling water dissolves coumaramine with facility; so likewise does boiling alcohol. An alcoholic solution saturated at a boiling heat, solidifies on cooling. Coumaramine is nearly insoluble in ether. It melts between 168° and 170° C., and when carefully raised to a higher temperature, gives off yellow vapours, which condense to pale yellow laminae. When coumaramine is quickly heated in a tube over a spirit-lamp, it turns brown, and distils over in the form of a heavy oil, which condenses to yellow crystals contaminated with a small quantity of an oil smelling like aniline.

The analysis of coumaramine yielded the following results, which agree with the formula $C_{18}H_7NO_4$.

	Found.				Calculated.
Carbon . .	67.5	67.3	—	C_{18}	67.08
Hydrogen .	4.3	4.5	—	H_7	4.34
Nitrogen .	—	—	9.1	N	8.69
				O_4	19.89
					<hr/> 100.00

Coumaramine unites readily with hydrochloric acid, forming a salt which dissolves readily in water, and crystallises in laminae. On adding ammonia to an aqueous solution of hydrochlorate of coumaramine, the liquid solidifies to a mass of crystals of coumaramine.

A boiling solution of caustic potash rapidly decomposes coumaramine. On neutralising the liquid with an acid, brown flakes are deposited.

On adding a solution of bichloride of platinum to a solution of hydrochlorate of coumaramine, a yellow crystalline precipitate is obtained, insoluble in water, and yielding by analysis 26.7 per cent. platinum. The formula $C_{18}H_7NO_4, HCl, PtCl_2$ requires 26.9.

Investigation of some Derivatives of Naphthallin.***By L. Dusart.**

If a mixture be prepared of 2 parts of caustic potash and 1 part of lime, moistened with water so as to form a thick paste, and 1 part of mononitronaphthalin be then added to the mixture by degrees, the mass immediately acquires a reddish-yellow colour, which is due to the formation of a peculiar acid. The mass is heated, for about six hours, to a temperature which must not pass $100^{\circ}\text{C}.$, with the addition from time to time of a few drops of water to replace that which is driven off. At the end of this time, the reaction is complete. The mass, washed by decantation until the water is no longer alkaline, is treated with an acid which separates the lime. The product thus obtained contains two matters, one yellow and crystallisable, the other brown and uncrystallisable. It is then distilled either by steam or by the open fire; the latter process is the more rapid, but furnishes a product of less purity, and in adopting it the operation must be stopped when red fumes begin to appear. The substance distilled forms crystals almost immediately.

This body, crystallised from boiling alcohol, furnishes long crystals of a straw-yellow colour; they are insipid, and of a weak aromatic odour. The substance fuses at $48^{\circ}\text{C}.$, boils at $290^{\circ}\text{C}.$, and passes over in great quantity at 300° to $320^{\circ}\text{C}.$, leaving a slight carbonaceous residue. It is very soluble in alcohol, ether, and the hydrocarbons. Boiling water dissolves a small quantity of it, and allows it to crystallise on cooling. A very concentrated solution of potash acts upon it, furnishing a yellow acid. When distilled with a mixture of potash and lime, it furnishes a yellow odoriferous oil and long needles, which communicate a fine violet-blue colour to sulphuric acid. The oily matter dissolves readily in water; a few drops of perchloride of iron added to the solution give it an intense blue colour, and blue flakes are soon precipitated; these are changed to red by alkalies. Sulphuric acid dissolves it with red colour. Sulphide of ammonium gives a new alkaloid.

Phthalidine, $\text{C}_{16}\text{H}_9\text{N}$.—This compound is produced by the action of sulphide of ammonium upon nitrophthaline. The action is greatly assisted by keeping the solution at a temperature of about $50^{\circ}\text{C}.$ on the water-bath for a few hours. After the alcohol has been driven off, the residue is exhausted by dilute muriatic acid, and filtered after cooling. Potash gives rise at first to a white precipitate, which is redissolved in the excess of acid with a fine blue colour; a greater quantity of potash separates the alkaloid in the form of flesh-coloured flakes, which soon change to red as they become aggregated. When

* Compt. rend. xli. 493.

washed and then crystallised by fusion, it is of the red colour of realgar; its odour resembles that of naphthalidine, and its taste is sharp and disagreeable.

It melts at 22°C . At the moment of solidification the thermometer rises to $34^{\circ}\cdot 5\text{C}$., when it remains stationary. It begins to boil at about 255°C ., but the temperature then rises rapidly, and the substance becomes partially altered, leaving a carbonaceous residue. It has no action upon reddened litmus, but its vapours immediately turn the litmus blue. It dissolves in ether and alcohol, and also in considerable quantity in cold water, from which it is deposited in long needles. Its aqueous solution precipitates the salts of suboxide and protoxide of mercury.

It reduces nitrate of silver. A few drops of sesquichloride of iron give a fine blue colour: this reaction, which is very delicate, is likewise exhibited by morphine and salicylic acid. It furnishes well-crystallised salts with all the acids. Bichloride of platinum reduces it when the solution of the hydrochlorate is diluted, furnishing blue flakes, which become black in drying. If the solution of the hydrochlorate is very concentrated, this reagent furnishes fine yellow crystals, which undergo a change in drying. The author was therefore unable to determine the equivalent by the analysis of the platinum-salt.

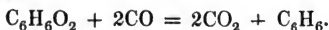
Nitrophthalinic Acid, $\text{C}_{32}\text{H}_{14}\text{NO}_{10}$.—Obtained in the preparation of the nitrophthaline, by a secondary reaction of the potash upon that body. It is then contaminated by a foreign substance, which is difficult to remove. It may be more advantageously prepared by treating pure nitrophthaline with a very concentrated solution of potash. Its formation is exceedingly slow.

The potash-salt obtained is treated with water, filtered, and decomposed by muriatic acid. The acid is crystallised from a mixture of 1 part of water and 2 of alcohol, of spec. grav. 0·848; it yields on cooling small golden-yellow crystals, grouped in stars. The acid is inodorous; its taste is scarcely perceptible at first, but afterwards becomes sharp. When heated in a tube, it fuses and leaves a carbonaceous residue.

The potash-salt is obtained by leaving the alcoholic solution to stand; it is deposited in small, reddish-yellow, mammellated crystals. It is very soluble in water, to which it gives a strong yellow colour. With nitrate of silver it forms a precipitate of a fine red colour; with acetate of lead, an orange-yellow precipitate; and a greenish-yellow precipitate with salts of copper. Most of its metallic salts explode on the application of heat.

Note on a New Mode of producing Propylene.***By L. Dusart.**

If a mixture of an alkaline acetate and oxalate be distilled in such a manner as to place the acetone formed in contact, when in the nascent state, with the oxide of carbon produced by the decomposition of the oxalate, deoxidation of the acetone takes place, with formation of a carbonate, and a gas passes which is absorbable by bromine, and which is nothing but propylene. The reaction may be represented by the following equation:—



Nevertheless we by no means obtain the quantity of propylene indicated by theory. The decomposition of the two salts is not simultaneous, and the oily matter observed in the preparation of acetone is always produced.

The process adopted is as follows:—Equivalent portions of acetate of lime and oxalate of potash are taken; the oxalate is dissolved in water, and the acetate of lime added to it, so as to produce oxalate of lime and acetate of potash. The liquid is evaporated, and kept in continual motion to obtain an intimate mixture. When dried as much as possible, the mass is put into a retort, which is heated over a moderate fire, and the quantity of propylene appears to be increased if the temperature be gradually and slowly raised. The gas passes first into a flask filled with carded cotton, then into a flask containing sulphuric acid, to absorb the oily matter; and it is afterwards condensed in bromine after being washed in water. A kilogramme of acetate of lime furnishes about 60 grms. of crude propylene.

The liquid obtained is washed with potash, and distilled directly; it is then agitated again with an alkaline solution, which saturates the hydrobromic acid formed during the distillation. It is dried over chloride of calcium, and distilled with a thermometer inserted.

Bromide of propylene forms about two-thirds of the product. It possesses the odour and the boiling-point (145°C.) of the propylene obtained from amylic alcohol.

The compound $\text{C}_6\text{H}_5\text{Br}$, obtained by the action of an alcoholic solution of potash upon the preceding product, when heated in a tube with sulphocyanide of potassium, furnished the essential oil of mustard, which has recently been produced by M. Berthelot with iodo-propylene obtained from glycerine. It is therefore possible by a simple deoxidation of acetone, to ascend from the acetic to the propylic series, and to reproduce the alcohol, if instead of collecting the hydrocarbon in bromine, we cause it to be absorbed by sulphuric acid, and distil it with water, according to the ingenious process of this chemist.

* Compt. rend. xli. 495.

On Tartrate of Lime and a Reaction of Tartaric Acid.***By A. Casselmann.**

THE author, when occupied in the examination of Alexandrian senna, found that the aqueous extract deposited the lime-salt of an organic acid on evaporation. This salt possessed a remarkable property; when gradually heated, after the addition of ammonia and nitrate of silver, it covered the sides of the test-glass with a metallic speculum of silver, in such a manner that the reaction may be compared with the reduction of nitrate of silver by aldehyde-ammonia. Even a very small quantity of the lime-salt was sufficient to reduce the nitrate of silver in the manner above mentioned, but only when the nitrate was added in small fragments, instead of in solution. If it were added in solution, the reduced silver was deposited in the form of a grey powder.

When the hot solution of the lime-salt was mixed with neutral acetate of lead, an abundant white precipitate was obtained, which, however, always contained traces of the lime-salt, unless the fluid were rapidly filtered whilst boiling. This precipitate was decomposed by sulphuretted hydrogen; the fluid containing the pure acid was evaporated, and the acid was obtained as a syrupy sharply acid fluid, which exhibited no trace of crystallisation, even after standing for several weeks.

The lead-salt of the acid was found to have the composition of tartrate of lead.

8 C	48.0	13.5	13.5
4 H	4.0	1.1	1.5
10 O	80.0	22.6	22.7
2 PbO	223.2	62.8	62.3
	<hr/> 355.2	<hr/> 100.0	<hr/> 100.0

Comparative experiments with artificially prepared tartrate of lime presented the same behaviour. The remarkable fact, that tartaric acid, in one of its least soluble compounds, possesses the property of instantaneously reducing nitrate of silver, might be made use of in analysis for the detection of minute traces of this acid. Racemic acid, however, gives the same reaction, and also produces it instantaneously, only when the nitrate of silver is added in the solid state.

Tartrate of lime occurs in considerable quantity in senna-leaves; but, from its sparing solubility, is not obtained from them without difficulty. The author has made experiments upon the solubility of tartrate of lime, and found that this salt requires for its solution 350 parts of boiling, and 1210 parts of cold water.

The author also boiled tartrate of silver with ammonia, to ascertain whether, as stated by Werther, a new ammoniacal salt is thus produced. He was unable to find anything of the kind.

* Arch. Pharm. lxxxiii. 148.

On Arabin.***By C. Neubauer.**

DURING an investigation of the ashes of various kinds of gums, Löwenthal prepared arabin by the process employed by Schmid, for the purification of tragacanth, &c. This process consists in dissolving gum-arabic in cold water, so as to form as thick a mucilage as possible, filtering, and adding hydrochloric acid till a strong acid reaction is produced, when the arabin is precipitated by means of alcohol; and these solutions and precipitations were repeated several times. The arabin, thus prepared in the form of a white amorphous mass, readily dissolves in water while still moist, forming a mucilage; the aqueous solution is not precipitated by alcohol, unless after the addition of hydrochloric acid or solution of chloride of sodium, when precipitation takes place immediately. The aqueous solution of pure arabin exhibits an acid reaction. When dried in the air, arabin becomes glassy and transparent, and gradually loses its solubility in water; when dried at 100°C ., it is no longer soluble in water, but only swells up in a gelatinous form in that fluid.

The composition of arabin, dried at 100°C ., agrees with the formula $\text{C}_{12}\text{H}_{11}\text{O}_{11}$; at a higher temperature it appears to give off no more water until it begins to decompose. Arabin, dried at 100°C ., and having an acid reaction, when mixed with lime-water until an alkaline reaction was produced, soon regained its acid reaction. From the fluid obtained by the action of lime-water upon arabin, alcohol separates a lime-compound, which readily dissolves in water forming a mucilage, and when dried at 100°C . has the formula $\text{CaO}, 6\text{C}_{12}\text{H}_{10}\text{O}_{10}$. From the fluid obtained by boiling arabin with water and an excess of hydrated lime, alcohol separates another lime-compound, which also dissolves readily in water: this, when dried at 100°C ., consists of $\text{CaO}, 2\text{C}_{12}\text{H}_{10}\text{O}_{10}$. By treating arabin with baryta-water (not in excess), and precipitating the liquid with alcohol, a baryta-compound is obtained, which when dried at 100°C . contains 11.0 to 11.2 per cent. of baryta. An excess of baryta-water furnished a compound containing 17.5 to 17.8 per cent. of baryta, the composition of which, when dried at 100°C ., approached very closely to the formula $\text{BaO}, 2\text{C}_{12}\text{H}_{10}\text{O}_{10}$. A potash-compound, precipitated by alcohol from a solution of arabin in potash, had the constitution $\text{KO}, 3\text{C}_{12}\text{H}_{10}\text{O}_{10}$ when dried at 100°C . Basic acetate of lead precipitates a lead compound from the aqueous solution of arabin; this becomes of a slight yellowish colour when dried at 100°C ., and of a strong brown at 160° to 180°C . Portions prepared at different times, and dried at 100°C ., contained 27.0, 30.5 to 30.8, and 30.5 to 30.7 per cent. of oxide of lead: the composition of the latter preparations approaches the formula $2\text{PbO}, 3\text{C}_{12}\text{H}_{10}\text{O}_{10}$.

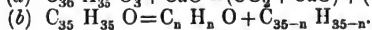
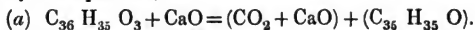
* J. pr. Chem. lxii. 193.

Examination of the Products of Distillation of pure Stearate of Lime.***By Prof. Heintz.**

Bussy states that the product of this operation is stearone,—a body which may be regarded as anhydrous stearic acid from which a number of equivalents of carbonic acid have been separated equal to the number of equivalents of base which it was capable of saturating. Rowney, however, has recently asserted that the solid fusible body formed is constituted according to the formula $C_{25}H_{29}O$. He calls it *stearene*.

From the results of the previous investigations of Heintz upon the products of the distillation of hydrated stearic acid, we may draw the conclusion that Bussy's view of the products of decomposition of stearate of lime is the correct one, and that it only requires correction in so far as the stearone formed is itself partially decomposed by the heat required for the decomposition.

The examination of the products of distillation of stearate of lime has shown that this conclusion is perfectly correct. The author found in this operation that the products were partly gaseous and partly solid. The former consist of hydrocarbons of the formula C_nH_n , and of light carburetted hydrogen, which is produced from the former by separation of carbon; the solid products consist of stearone ($C_{35}H_{35}O$), and other ketones, which are produced along with the hydrocarbons by the decomposition of the stearone. The decomposition may be expressed by the equations,—



The author obtained pure stearone by repeated extraction of the above-mentioned products of distillation with alcohol, and recrystallising the undissolved portion from its solution in boiling ether. It possessed all the properties of that produced by the distillation of hydrated stearic acid, but its melting-point was a little higher, namely $87^{\circ}.5$ C.; evidently in consequence of its greater purity.

To determine the atomic weight of stearone, the author prepared a product of substitution by means of bromine, which he found to be constituted according to the formula $C_{35}\left\{\begin{smallmatrix} H_{34} \\ Br \end{smallmatrix}\right\}O$.

From the analysis of the portion of the crude stearone, which was soluble in alcohol, it appeared to contain the same number of equivalents of hydrogen and carbon, but a larger amount of oxygen, showing that it contained (perhaps together with stearone) other ketones with a smaller amount of carbon and hydrogen.

* Wien Akad. Ber. 1855, 385.

TITLES OF CHEMICAL PAPERS

IN

BRITISH AND FOREIGN JOURNALS,

PUBLISHED IN THE YEAR 1855.

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- I.—Chemical examination of mangold-wurzel, p. 1.
 - II.—Chemical composition of red and black clover (*Trifolium pratense* and *Trifolium hybridum*) at different stages of growth, p. 8.
 - III.—Alteration of red clover hay by washing with rain, p. 13.—Influence of manuring with ashes and gypsum on the chemical composition of clover, p. 15.
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